ORGANO-NITROGEN COMPOUNDS OF COBALT

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of

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by

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ABSTRACT

The reactions of cobalt halides with lithium dialkylamides have been investigated. The reaction with lithium diethylamide proved to be very unusual. This reaction was fully studied and the main products were shown to be lithium chloride, cobalt metal and bis(4-ethylimino-2-butene-2-ethylamino)cobalt(II). The latter product which was a volatile brown liquid was identified by its physical and chemical properties and the physical properties of derivatives prepared from the ligand after removal of the cobalt.

Bis-(4-ethylimino-2-butene-2-ethylamino)cobalt(II) is a nitrogen analogue of the metal acetylacetonates and shows many similar properties. The ligand 4-ethylimino-2-ethylamino-2-butene was shown, by the magnetic moment and electronic spectra of the tetrahedral cobalt compound, to produce a very high ligand field.

A reaction mechanism has been proposed to explain the products of the reaction of cobalt chloride with lithium diethylamide.

The reactions of other lithium dialkylamides with cobalt halides have shown that dialkylamino compounds of cobalt(II) exist but are generally unstable thermally and very oxygen sensitive. The only stable (thermally) dialkylamino cobalt(II) compound prepared was bis-hexamethyldisilylamino cobalt(II). In solution this compound was shown to be a linear two coordinate compound of cobalt(II). This unusual stereochemistry for cobalt(II) presents many theoretical problems before the magnetic and spectral properties are fully understood.

It was found that the other dialkylamino cobalt(II) compounds produced were unstable, thermally decomposing above room temperature. The most stable compounds were formed when the dialkyl- group produced large steric hindrance.

Two new alkoxides were prepared from the dialkylamino cobalt(II) compounds. The magnetic and spectral properties of these compounds indicate that they are polymeric, possibly three coordinate compounds of cobalt.

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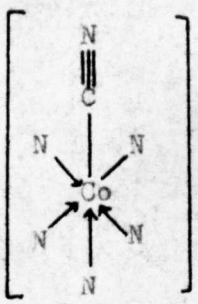
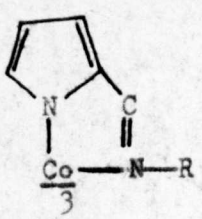
INTRODUCTION

This thesis is concerned with the preparation, chemical and physical properties of cobalt compounds of organic secondary amines and derivatives of these amines. Many compounds of cobalt are known where the amine (N-H) hydrogen has been replaced by cobalt. These are generally not simple aliphatic or aromatic amines but derivatives of amines containing another atom which can coordinate with the metal. A few examples of these compounds are given below.

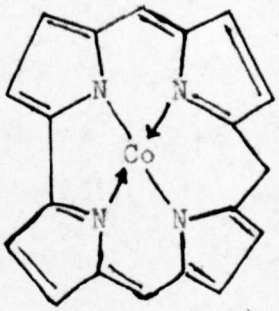
One very important compound of this general type which occurs naturally is vitamin B_{12} which is a compound of cobalt (III). The cobalt aton is surrounded by five nitrogens and a cyanide group with the stereochemistry of the cobalt atom as shown below:-



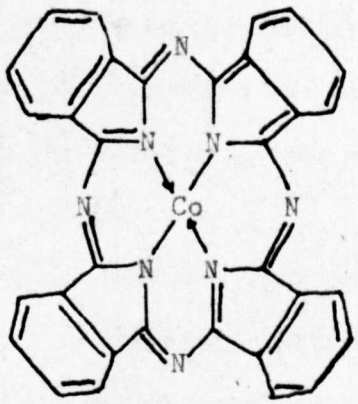
Pyrrole compounds of which vitamin B_{12} is one constitute another important type. One of the simplest of this type is the octahedral cobalt (III) compound formed by amines of pyrrole-2-aldehyde[1].



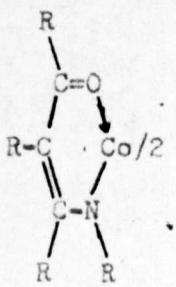
Others of this general type are compounds related to the porphins e.g. The cobalt complex shown on page 2.



Cobalt phthalocyanine is also a related compound (this will be discussed later in the thesis but the structure is shown below).



β-Ketoamine compounds of cobalt have been prepared by Everett and Holm[2] and the secondary amine derivatives shown by the general structure below are tetrahedral.



There are other known compounds of this type but the preceding examples show that the metal to nitrogen bond formation is helped by the coordination of oxygen or nitrogen to the cobalt. Although

no simple secondary amine compounds of cobalt have been reported, other metals have been shown to form simple dialkyl- or diaryl-amino compounds. The only simple aliphatic secondary amine complexes of cobalt reported in any detail are the diethylamine complexes of the halides[3]. Anhydrous cobalt halides were shown to react with diethylamine to form pseudotetrahedral complexes $CoX_2\left[(C_2H_5)_2NH\right]_2$. Magnetic and spectral measurements were used to identify the tetrahedral stereochemistry. The importance of these measurements in the determination of the stereochemical enviroment of the cobalt atom will be discussed later in this introduction. These compounds have the amine coordinated by the nitrogen to the cobalt but there had been no displacement of the hydrogen on the nitrogen by the cobalt.

The history of metal amine compounds started in 1857 when Frankland[4] was investigating the chemical reactions of zinc diethyl. He caused zinc diethyl to react with several amines and obtained compounds which included zinc diethylamide $Zn\left[N(C_2H_5)_2\right]_2$. In 1897 Titherly[5] reported that sodium amide reacts with primary and secondary amines with replacement of one hydrogen and thus he was able to prepare sodium phenylamide and sodium diphenylamide. The lithium derivatives were prepared by Ziegler et.al. in a series of papers and patents in the 1930's[6,7,8,9,10]. The general method used was the reaction of an organo lithium derivative e.g. phenyl lithium with an amine.

Some of the lithium amides show properties which definitely

indicate a metal-nitrogen covalent bond rather than an ionic formulation. Lithium di-isopropylamide is soluble in non-polar organic solvents. In the absence of molecular weight data in solution one must assume that these compounds are similar to the lithium alkyls[11] and lithium alkoxides[12].

Many other elements have been shown to form dialkylamino compounds. Boron trihalides will react with some secondary amines to form tris-dialkylamino compounds of boron[13]. Using this method Lappert et.al. were able to prepare the lower n-alkyl derivatives (dimethyl, diethyl and di-n-butyl) but replacement of only two chlorines was effected by diphenylamine and di-isopropylamine. The tetrakisdimethylamide derivative of carbon has been prepared[14]. Aluminium which has a covalent radius of 1.25 $\mathring{A}$ as compared with boron having a covalent radius of 0.8 $\mathring{A}$ is able to form a tris-di-isopropylamide[15]. Silicon forms a tetrakisdiethylamide under very drastic condition i.e. heating tris(diethylamino) bromosilane with diethylamino magnesium bromide at 150°C[16]: the dimethylamide and the tetrapiperidino compounds have also been prepared[17], The tetrakisdiethylamino derivative of germanium has been prepared by the reaction of germanium tetrabromide with diethylamine[18]. The dimethylamino derivatives of phosphorus[19], sulphur[20], arsenic[21] and antimony[22] have also been prepared.

Tin dialkylamides were first prepared by Thomas[23] by the reaction of tin tetrachloride with lithium dialkylamides. The preparations of organotin dialkylamides has been well documented and are excellently reviewed by Jones and Lappert[24].

The study of dialkylamino and diarylamino compounds of transition metals started in 1935 when Dermer and Fernelius[25] caused potassium

diphenylamide to react with titanium tetrachloride, thus synthesizing titanium IV tetradiphenylamide. Gilman et.al.[26] prepared uranium IV tetradiethylamide by distilling the product of the reaction of uranium tetrachloride with lithium diethylamide. Other secondary amines were tried but no other dialkylamides could be distilled and even diethylamide seemed to be thermally unstable unless a very low pressure was used for the distillation. Bradley and Thomas prepared the dialkylamides of titanium and zirconium[27], niobium[28] and tantalum[29] by the reaction of the metal halides with lithium dialkylamides of titanium and zirconium were all monomeric except zirconium dimethylamide which was found to have a degree of polymerization of 1.22. These compounds react vigorously with water and with alcohols produce alkoxides. Aminolysis with other secondary amines was carried out but it was found that with amines producing large steric effects such as di-isopropylamine only partial substitution could be obtained even with zirconium.

Niobium and tantalum provided some interesting results. Firstly, niobium (V) chloride when caused to react with lithium dimethylamide gave a volatile penta-dimethylamide. All other secondary amines tried except N-methyl-n-butylamine gave volatile niobium (IV) dialkylamides. Even the N-methyl-n-butylamide was thermally unstable distilling to give a product which appeared to be predominantly tetrakis (N-methyl-n-butylamino) niobium (IV). Thus in all cases, except with dimethylamine, there had taken place a reduction from niobium (V) to niobium (IV).

$$Nb(NR_2)_5 \longrightarrow Nb(NR_2)_4 + NR_2 \ (-HNR_2 + \text{imine etc.})$$

Tantalum proved to be slightly different, firstly a penta-dimethylamide could be sublimed in vacuo and pentakis derivatives $Ta(NR_2)_5$ (where R=Et, Pr^n, Bu^n) also $Ta(NMeBu^n)_5$ and $Ta(NC_5H_{10})_5$ were prepared in an impure state without distillation. Attempted distillation to purify these compounds resulted in thermal decomposition according to the following equation.

$$Ta(NR_2)_5 \longrightarrow RN{=}Ta(NR_2)_3 + R_2NH + \text{Olefin (e.g. } CH_2 = CH_2)$$

The tantalum compounds so produced still have a valency of five but on hydrolysis or alcoholysis, they give off primary amine and secondary amine in the ratio 1:3. Further work using N.M.R.[30] has shown that in the compound $EtN{=}Ta(NEt_2)_3$ there are two distinct types of ethyl groups.

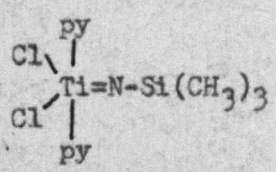
Basi and Bradley have prepared some dialkylamides of chromium (III)[31] and chromium (IV)[32]. The compound $Cr(NPr^i)_3$ is a black sublimable solid which is very sensitive to oxygen and easily hydrolysed. It has been used to prepare pure alkoxides of chromium (III). $Cr(NEt_2)_4$ is a green volatile liquid produced on the attempted distillation of the products of the reaction of chromium trichloride and lithium diethylamide. This compound is also easily hydrolysed.

Wannagat and Bürger while investigating the properties of lithium bis-trimethylsilylamide prepared bis-trimethylsilylamino derivatives of chromium (III)[33], manganese (II)[33], nickel (II)[33], copper (I)[33], titanium[34], vanadium[35], zinc[36], cadmium[36], iron (III)[37] and cobalt (II)[37].

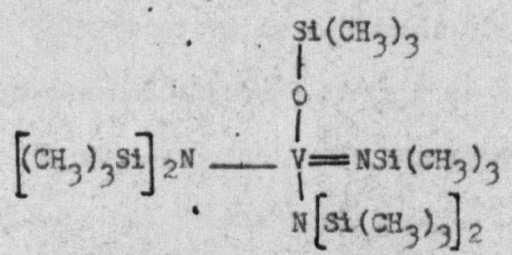
The bis-trimethylsilylamino derivatives of chromium, manganese, nickel and copper, were produced by the reaction of sodium bis-trimethyl

silylamide with $CrCl_3$, MnI_2, NiI_2 and CuI, respectively. All of these compounds were found to be volatile and could be sublimed in vacuo. They appeared to be reactive towards oxygen.

Titanium tetrachloride gave only a mono-substituted derivative when caused to react with sodium bis-trimethylsilylamide. $TiCl_3N-(Si(CH_3)_3)_2$ reacted with pyridine giving a product formulated by Wannagat as:-



Trimethylchlorosilane was shown to be the other product of this reaction. Vanadium oxychloride when reacted with sodium bistrimethylsilylamide was said to produce the compound:-



This was identified by its chemical properties, infrared spectrum and N.M.R. spectrum. The latter gave three sharp signals in the ratio 1:2:3 Wannagat rationalized this by postulating that the $-N\left[Si(CH_3)_3\right]_2$ groups were non-equivalent and one of the signals produced was superimposed upon one of the other signals.

These titanium and vanadium compounds obviously need more study. The properties of a metal nitrogen double bond proposed in these compounds and $EtN=Ta(NEt_2)_3$ should be very interesting.

The zinc, cadmium and mercury compounds were prepared in a similar

manner. The infrared and Raman spectra of these compounds were shown by a normal coordinate analysis, including the silicon, nitrogen and metal atoms, to correspond to D_{2h} symmetry. Thus all the atoms mentioned lie in a plane and the nitrogen-metal-nitrogen bonds are linear. The symmetrical and asymmetrical stretching modes of the metal-nitrogen bonds were assigned as follows:-

M	$\nu_{as}(MN_2)$	$\nu_{s}(MN_2)$
Zn	436	400
Cd	410	385
Hg	406	390

The bis-trimethylsilyl derivatives of iron (III) and cobalt (II) were prepared in a similar manner. The iron compound was shown to be monomeric and soluble in non-polar organic solvents. The cobalt compound is the only reported dialkylamide of cobalt and as such warrants a preliminary discussion although it will be dealt with further in the thesis. Wannagat found that with tetrahydrofuran as solvent he could prepare cobalt bis-trimethylsilylamide in approximately 50% yield. This compound could be distilled and he predicted that from the boiling point (101° at 0.6 mm Hg pressure) that it was monomeric in the vapour state. The compound crystallizes as green needles which turn black when exposed to oxygen. The compound appeared to be very susceptible to hydrolysis as well as oxygen. Wannagat showed by full elemental analysis that there was no molecule coordinated to the cobalt such as tetrahydrofuran or hexamethyldisilazane. It is freely soluble in non-polar solvents.

The aforementioned dialkylamino compounds have certain important

properties which need to be outlined. The most important reactions are (a) substitution and (b) addition.

$$(a)\ M\text{-}N< + HX \longrightarrow M\text{-}X + HN<$$

$$(b)\ M\text{-}N + X{=}Y \longrightarrow M\text{-}X\text{-}Y\text{-}N<$$

These reactions have been reviewed for tin compounds by Jones and Lappert[24] and most other dialkylamino metal compounds give similar reactions. A few examples of relevance to this thesis are given below:-

(a) 1. Reaction with water (hydrolysis)

$$M(NR_2)_x + x\ H_2O \longrightarrow M(OH)_x + HNR_2$$

2. Reaction of alcohols forming alkoxides

$$M(NR_2)_x + x\ ROH \longrightarrow M(OR)_x + x\ RNH_2$$

3. Reactions with primary amines

$$M(NR_2)_x + x\ RNH \longrightarrow M(NHR)_x + x\ RNH_2$$

The primary examples of (b) are the reactions with CS_2 and CO_2 to form dialkyldithiocarbamates and dialkylcarbamates respectively.

$$M(NR_2)_x + xCS_2 \longrightarrow M(SCSNR_2)_x$$

Cobalt is element 27 and is in Group VIII of the Periodic Table. Cobalt has the electronic configuration in the ground state of $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^7$, $4s^2$. It exhibits several valency states e.g. -1, 0, 1, 2, 3 and 4. The stability and stereochemistry in these valency states is determined by the ligands.

An example of the stability of the oxidation states 2 and 3 with different ligands is shown by the oxidation-reduction potentials of the following complex systems in aqueous solution.

Complexes	Oxidation-Reduction Potentials
$\left[Co(H_2O)_6\right]^{2+} / \left[Co(H_2O)_6\right]^{3+}$	+ 1.84 volts.
$\left[Co(NH_3)_6\right]^{2+} / \left[Co(NH_3)_6\right]^{3+}$	+ 0.10 volts.

The potential for the cobalt (III) aquo complex is so high that it will accept an electron from the hydroxyl ion in solution and become cobalt (II). The ammine complex is quite different and $\left[Co(NH_3)_6\right]^{2+}$ is oxidized by atmospheric oxygen to $\left[Co(NH_3)_6\right]^{3+}$.

As this thesis is mainly concerned with cobalt in its oxidation state of two the following discussion of stereochemistry will mainly cover cobalt (II) with some references to cobalt (III). An exellent review article by Carlin[38] discusses the electronic structure and stereochemistry of cobalt (II). Another article by Lewis[39] discusses the spectroscopic and magnetic properties of complexes of cobalt (II).

The two main stereochemistries of cobalt (II) are tetrahedral and octahedral, cobalt (III) complexes are almost invariably octahedral. The factors influencing coordination are not yet fully understood but some ligands impose a particular stereochemistry upon the cobalt, e.g. the phthalocyanine and porphyrin complexes are square planar. There may often be an equilibrium between two stereochemistries e.g.

$$Co\ py_2\ X_2 + 2py \rightleftharpoons Co\ py_4 X_2$$

Tetrahedral Octahedral

Five coordination has been shown to be increasingly common amongst cobalt compounds. Thus $Co(NO)\left[S_2C(CH_3)_2\right]_2$ has been shown by crystal structure to be a rectangular-based pyramidal structure[40].

Eight coordination has been shown to exist in a few compounds, a good example is $\left[As(C_6H_5)_4\right]_2Co(NO_3)_4$[41]. Ideal tetrahedral and octahedral symmetries do not exist, there always seems to be some distortion present.

The $(CoCl_4)^{2-}$ anion has angles of 107° 20′, 108° 50′, 109° 20′ and 116° 20′ in Cs_2CoCl_4. Thus all the compounds which are called tetrahedral or octahedral are really only 'pseudo' tetrahedral or octahedral.

The magnetic and spectral properties of cobalt complexes are often diagnostic of the presence of octahedral or tetrahedral stereochemistry. Simplified energy level diagrams for a d^7 ion in octahedral and tetrahedral fields are shown in Figs 1 and 2.

The ground state for octahedral d^7 complexes is either $^4T_{1g}(t_{2g})^5(e_g)^2$ or $^2E_g(t_{2g})^6(e_g)^1$, depending upon the strength of the ligand field. In weak ligand fields the $^4T_{1g}$ state is the ground state and so in $\left[Co(H_2O)_6\right]^{2+}$ which gives a band at 8350 cm^{-1} and a band system at approximately 20,000 cm^{-1} the former is assigned the $^4T_{1g} \longrightarrow {}^4T_{2g}$ and the latter $^4T_{1g} \longrightarrow {}^4T_{1g}(P)$. The transition $^4T_{1g} \longrightarrow {}^4A_{2g}$ is a two electron transition and so should only have a very small intensity and this has been identified at 17,850 cm^{-1} [42].

The ground state for tetrahedral complexes of cobalt (II) is $^4A_2(F)$. The first transition (ν_1) occurs at 10 Dq and is assigned to $^4A_2(F) \longrightarrow {}^4T_2(F)$ The second transition (ν_2) is $^4A_2(F) \longrightarrow {}^4T_1(F)$ and the third (ν_3) is $^4A_2(F) \longrightarrow {}^4T_1(P)$. The first transition ν_1 should occur between about 3000 cm^{-1} and 5000 cm^{-1} but it has been little observed. The second and third transitions are of much greater intensity and are generally observed in the regions 5000 cm^{-1} to 8000 cm^{-1} and 15,000 cm^{-1} to 20,000 cm^{-1} respectively. A few examples are given in table 1 from work by Cotton[43].

As well as the band positions being a guide to stereochemistry the band intensity are also important. Generally band intensities are

Fig 1.

Simplified energy level diagram for a octahedral d^7 ion.

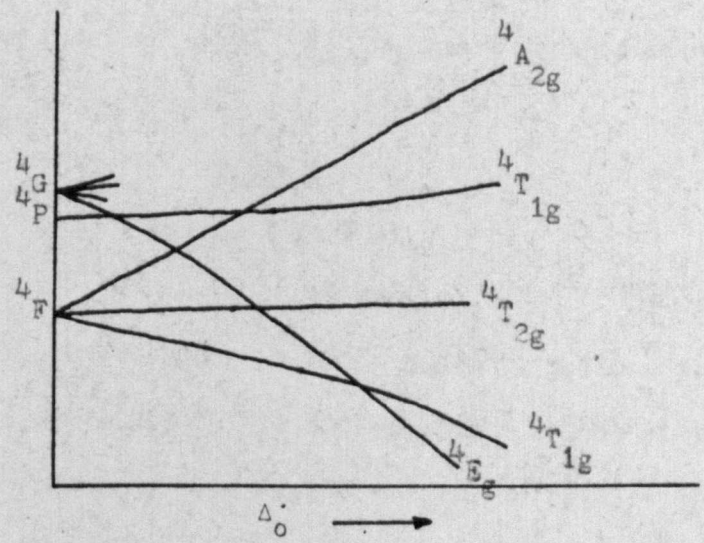
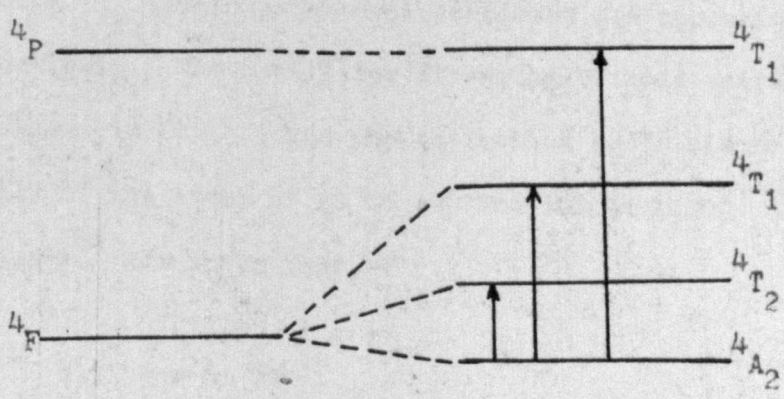


Fig 2.

Simplified energy level diagram for a tetrahedral d^7 ion.



measured by the molar extinction coefficient but this is less important than the oscillator strength f, which is given by $f = 4.32 \times 10^{-9} \int \epsilon d\nu$ where ν is the frequency of the band. If the band is assumed to be a Gaussian curve then $f = 4.60 \times 10^{-9} \epsilon_{max} \nu_{\frac{1}{2}}$ where $\nu_{\frac{1}{2}}$ is the band width where $\epsilon = \frac{1}{2} \epsilon_{max}$.

Table 1

Ligand X in $(CoX_4)^{2-}$	I^-	Br^-	Cl^-	NCS^-
ν_2 cm^{-1}	4,500 - 4.700	4,880 - 5.080	5,220 - 5.700	7.780
ν_3 cm^{-1}	13,000 -13,500	13,800 -14,200	14,600 -14,800	16,250
10 Dq cm^{-1}	2,590 - 2,700	2,790 - 2,910	2,985 - 3,275	4,550
$f(\nu_2)$ $cm^{-1} \times 10^3$	1.11	0.71	0.72	3.55
$f(\nu_3)$ $cm^{-1} \times 10^3$	8.12	5.89	5.09	14.60
μ_{eff} B.M.	4.77	4.69	4.59	4.40

Generally, the extinction coefficients and oscillator strengths for the transition $^4T_{1g} \longrightarrow {}^4T_{1g}$ (P) in octahedral complexes are approximately 10 and 2×10^{-4} respectively. The oscillator strengths of some tetrahedral complexes are shown in Table 1 and the extinction coefficients of ν_2 and ν_3 are generally of the order of 50 to 100 and 100 to 1,000 respectively. Ballhausen[44] has shown that,

$$\frac{f(\nu_3)}{f(\nu_2)} \approx 10$$

The magnetic properties of Co^{2+} have been well studied and the paramagnetic susceptibility of Co (II) was originally explained by Schlapp and Penney[45].

The spin-only moment for cobalt (II) is 3.88 B.M.

$$\mu^2_{eff} = \beta^2 g^2 S(S + 1)$$

Where $S = {}^3/_2$ $g = 2.0023$.

The spin-only moment has not been found for tetrahedral or octahedral Cobalt (II) compounds. In the octahedral case the ground state $^4T_1$ is orbitally degenerate and causes an angular momentum contribution to the magnetic moment. Thus the moment lies between the limits of the spin-only moment 3.88B.M. and

$$\mu = \left[4S(S + 1) + L(L + 1)\right]^{\frac{1}{2}} = 5.2\text{B.M.}$$

S is the spin-angular momentum ${}^3/_2\hbar$ and L is the total orbital angular momentum $3\hbar$. The experimental moments lie between 4.7 and 5.2 B.M.

A few spin-paired octahedral complexes have been measured and these generally have moments between 1.8 and 1.9 B.M.. The slightly high moment (1.73 B.M. for one unpaired electron), is caused by spin-orbit coupling. Tetrahedral complexes always have magnetic moments higher than the spin-only moment caused by spin-orbit coupling. Spin-orbit coupling causes the mixing of the $^4F_1$ and $^4T_2$ states with the ground state. The spin-orbit coupling decreases as the separation of the states from the ground increases. Therefore high ligand fields which cause high values of 10Dq have the lowest moments. Generally the moments of tetrahedral complexes are in the range 4.4 - 4.7 B.M..

Square planar complexes of cobalt (II) generally exhibit moments higher than the spin-only moment for one unpaired electron. The phthalocyanine gave a value of 2.72[46] at room temperature but showed a temperature dependence giving a moment of 2.22 at 90°K.

Five coordinate complexes of cobalt which have been investigated generally give moments of the order 2.2 - 2.5 B.M..

It may be seen from the preceding summary that the stereochemistries of cobalt (II) have been thoroughly investigated and a combination of the spectral and magnetic properties may often be used in identifying a specific stereochemistry. This method has been used for identification of some of the stereochemistries of compounds produced in this thesis.

Bradley and Thomas[47] carried out reactions of metal halides of the first transition series with lithium diethylamide. As stated previously, the reactions with titanium, vanadium and chromium proceeded smoothly to give metal diethylamides. For the later transition metals the reaction was not straight-forward and some products were obtained which did not have properties characteristic of metal dialkylamides. Manganese (II) chloride, iron (III) chloride, cobalt (II) chloride and nickel (II) chloride were all caused to react with lithium diethylamide and upon distillation of the reaction products a yellow or orange oil was obtained. This distillation product was generally less than ten per cent by weight of the total products of the reaction. In each case the product was notably resistant to hydrolysis (in contrast to metal dialkylamides). Also they all exhibited a strong ultravoilet absorption in the region of 300 mμ ($\sim$33,000 cm^{-1}) and a strong absorption in the infrared at approximately 1560 cm^{-1}. The cobalt and nickel systems were investigated more fully than the others.

The reaction between cobalt chloride and lithium diethylamide was carried out in several solvents, it was shown that using either diethylamine or tetrahydrofuran as solvent and a ratio of Co:Li of 1:4

up to 12% of distilled product (based on weight of cobalt chloride taken) could be obtained. The reaction did not appear to proceed below $-20^{\circ}C$. The distilled product (a brown liquid) gave variable chemical analyses but the compound was purified by fractional distillation and gave a cobalt to nitrogen ratio of 1:4. A molecular weight was obtained in cyclohexane of 332 ± 10 and magnetic moment giving a value of $\mu_{eff} = 3.9$B.M. was obtained. The infrared, ultravoilet and visible spectra were obtained and the assignment of the infrared band at 1560 cm^{-1} was tentatively assigned to "C=N possibly conjugated". The spectral and magnetic properties pointed to tetrahedral cobalt surrounded by four nitrogens. Some chemical reactions were tried but most gave inconclusive results as to the structure of the compound. Two methods were found for extracting the cobalt from the ligand.

1. An ion-exchange method using an anion-exchange resin. The compound was dissolved in 8N hydrochloric acid and treated with anion-exchange resin to remove the $(CoCl_4)^{2-}$ formed leaving the ligand in solution as the hydrochloride.
2. Precipitation of the cobalt as the benzimidazole complex leaving the ligand. These methods will be discussed later in the thesis.

It was felt worthwhile investigating this compound in more detail so that a structure could be assigned. The reactions of other dialkylamides with cobalt halides was also undertaken with the object of preparing similar compounds or possibly dialkylamides of cobalt.

The disilylamide of cobalt was also investigated as this was the only known dialkylamide of cobalt. Wannagat had predicted that from the

volatility this compound was probably monomeric in the vapour phase. This unique stereochemistry (if correct) would be of very great importance and should lead to unusual physical and chemical properties.

EXPERIMENTAL and RESULTS.

1. Apparatus & General Procedure

The sensitive nature of the compounds produced especially to water and/or oxygen necessitated the use of a very stringently dry and oxygen-free atmosphere. Because of the very low volatility of the compounds a normal vacuum system could not be used. All glass apparatus was used wherever possible. This was dried in an oven at 140°C for several hours before use. The apparatus was evacuated whilst hot and filled with purified nitrogen. The nitrogen (British Oxygen 'White Spot') was deoxygenated by passing through a solution of the sodium ketyl of benzophenone and then through a column containing B.T.S. catalyst heated to about 140°C. The drying was carried out by passing the nitrogen through phosphorus pentoxide then Linde "molecular sieves" type 5A drying reagent.

2. Drying of solvents

Benzene, cyclohexane, n-pentane, n-hexane and diethylamine and other dialkylamines were stored over sodium wire and distilled from fresh sodium then stored over "molecular sieve" type 3A under a nitrogen atmosphere.

Tetrahydrofuran was dried by distilling from calcium hydride and stored over "molecular sieve" type 3A drying reagent.

Alcohols used except methyl alcohol were azeotropically dried with benzene and stored over "molecular sieves" type 3A drying reagent. Methyl alcohol was dried by refluxing over magnesium methoxide and subsequent distillation. The magnesium methoxide was made in situ by treating the methyl alcohol with magnesium turnings and a crystal

of iodine.

Solvents were degassed under vacuum whenever required. Cobalt halides were dried by heating the hydrates under vacuum at 140°C. Thionyl chloride was added to cobalt chloride when it was pale blue and this removed the last traces of moisture. Excess thionyl chloride was removed after refluxing for a short while.

3. Analytical Methods.

Cobalt was determined by two main methods which gave consistent results. After preliminary oxidation with nitric acid or dissolution with hydrochloric acid (the latter being preferred) the cobalt was determined either gravimetrically as the cobalt pyridine thiocyanate[48] or volumetrically using E.D.T.A. by the method of Sarma[49].

Chlorine was determined either gravimetrically as silver chloride or volumetrically by Volhard's method. Nitrogen was determined by the Kjeldahl method. Some secondary amines were determined by hydrolysis of the sample and then distillation from a strongly alkaline solution into excess standard acid solution. The excess acid was titrated with standard alkali solution. Carbon hydrogen and nitrogen analyses were determined by A. Bernhardt, Mulheim, Germany.

4. Instrumental Methods

Infrared (I.R.) spectra were recorded in the region 4000 cm^{-1} to 400 cm^{-1} with a Perkin-Elmer 337 Grating Spectrophotometer. Nujol mulls and pure liquids were placed between potassium bromide plates in this region and solution spectra were taken using cells with potassium bromide windows. Spectra in the region 500 cm^{-1} to 200 cm^{-1} were conducted on a Grubb Parson DM 4 Grating Spectrophotometer using polythene plates. Reactive compounds were handled in a dry box or in

solution and kept under nitrogen atmosphere using syringes.

Ultravoilet, (U.V.) visible and near I.R. spectra were carried out on a Beckman DK 2A recording spectrophotometer. Solution spectra were generally obtained in 1 cm, path length cells fitted with C 10 quickfit cones and C 10 sockets used as caps. Pure liquids and nujol mulls were occasionally used between thin glass plates in the region 350 mμ to 1700 mμ.

Proton Nuclear Magnetic Resonance (N.M.R.) spectra were obtained using either a Varian A.60 or a Varian HA & HR 100 operating at 60 Mc/s and 100 Mc/s respectively.

Molecular weight determinations were carried out cryoscopically in cyclohexane using a thermistor (as one arm of a Wheatstone Bridge) to measure the temperature changes. The imbalance of the bridge was measured on a Kelvin Potentiometric Recorder. A special cell was used so that additions could be made under nitrogen in completely dry conditions. Fluorene was used to standardize the system when cyclohexane was used as solvent.

Magnetic susceptibilities were measured on a "Newport Variable Temperature Gouy Balance". Measurements were made at two or more magnetic fields to check for ferromagnetic impurities (shown by field dependences of the susceptibility). Mercury tetrathiocyanatocobaltate and aqueous nickel chloride solutions were used as calibrants for the tubes. Silica tubes with B5 sockets were used so that samples could be kept under nitrogen. Samples of 10 cm length were used and these gave reliable results. Samples of less than 8 cm. length were found to give unreliable results.

The reaction of cobalt chloride with lithium diethylamide

This reaction was carried out in a variety of solvents as shown in Table 2 but the experimental details will be described for diethylamine as solvent.

Lithium diethylamide was prepared by the reaction of n-butyllithium with diethylamine at 0°C. After addition of 10 per cent excess diethylamine needed for reaction, the solvent was removed under vacuum. Diethylamine was then added which dissolved the lithium diethylamide giving a clear pale yellow solution. Cobalt chloride was then carefully added. This gave an exothermic reaction the colour of the solution changing first to blue, then to green and finally, black. The solution was refluxed and stirred for several hours. The solvent was then removed in vacuo. The residue was extracted with pentane or hexane and the solution filtered and evaporated to dryness. The pentane extract was then heated under reduced pressure and at 120° to 130° /0.1 mm. Hg a brown liquid was distilled (compound A).

Table 2 shows that the best yields were obtained by using a molar ratio of cobalt chloride to lithium diethylamide of 1:4. The yield of distilled compound is based upon the weight of cobalt in the distilled product compared with the weight of cobalt chloride used.

Two reactions were tried using sealed tubes. These were cooled in liquid nitrogen while opening into a vacuum system. No noncondensable gas was observed upon opening the tubes.

Table 2

Solvent	Temp °C	Stirring Period	Wt. of $CoCl_2$	Ratio of $CoCl_2$:$LiNEt_2$	Yield (g)	Yield %
* Diethylamine	Boiling Solvent	12 Hrs	30 g.	1:1	0.0	0.0
* n-Hexane	60°C	12 Hrs	-	1:2	-	0.9
* Ether	Boiling Solvent	24 Hrs	-	1:2	-	4.8
* Diethylamine	" "	12 Hrs	-	1:2	-	6.3
Diethylamine	" "	100 Hrs	18.5 g.	1:2	3.3	6.9
Diethylamine + pentane	" "	48 Hrs	52.6 g.	1:2	8.1	6.0
Diethylamine	" "	100 Hrs	8 g.	1:3	1.2	5.8
Diethylamine	" "	24 Hrs	5.9 g.	1:4	1.6	10.5
Tetrahydrofuran	" "	24 Hrs	18 g.	1:4	5.6	12.0
* Diethylamine	" "	16 Hrs	22 g.	1:4	8.0	14.0
* Tetrahydrofuran	" "	28 Hrs	15 g.	1:4	4.5	11.6

*Results from reference 47

Examination of the products of the reaction

The pentane insoluble portion was washed with diethylamine and analysis and X-ray powder photography showed this product to be mainly lithium chloride. The pentane soluble product was examined after distillation. A typical analysis of this black tar-like residue, after a reaction of 1 mole of cobalt chloride with lithium diethylamide (2 moles) had taken place, gave a cobalt analysis of greater than 50% plus a small percentage of lithium. Commercial analyses for carbon, hydrogen and nitrogen were generally unsuccessful or erratic. After washing with diethylamine and careful filtration, a black fine powder was obtained. This gave a very high cobalt analysis (approx. 80% to 90%). There was also a little lithium and chloride present. X-ray powder photography showed the presence of cobalt metal and possibly some non-crystalline material that gave no lines but a general dispersion of the X-rays causing a darkening of the film.

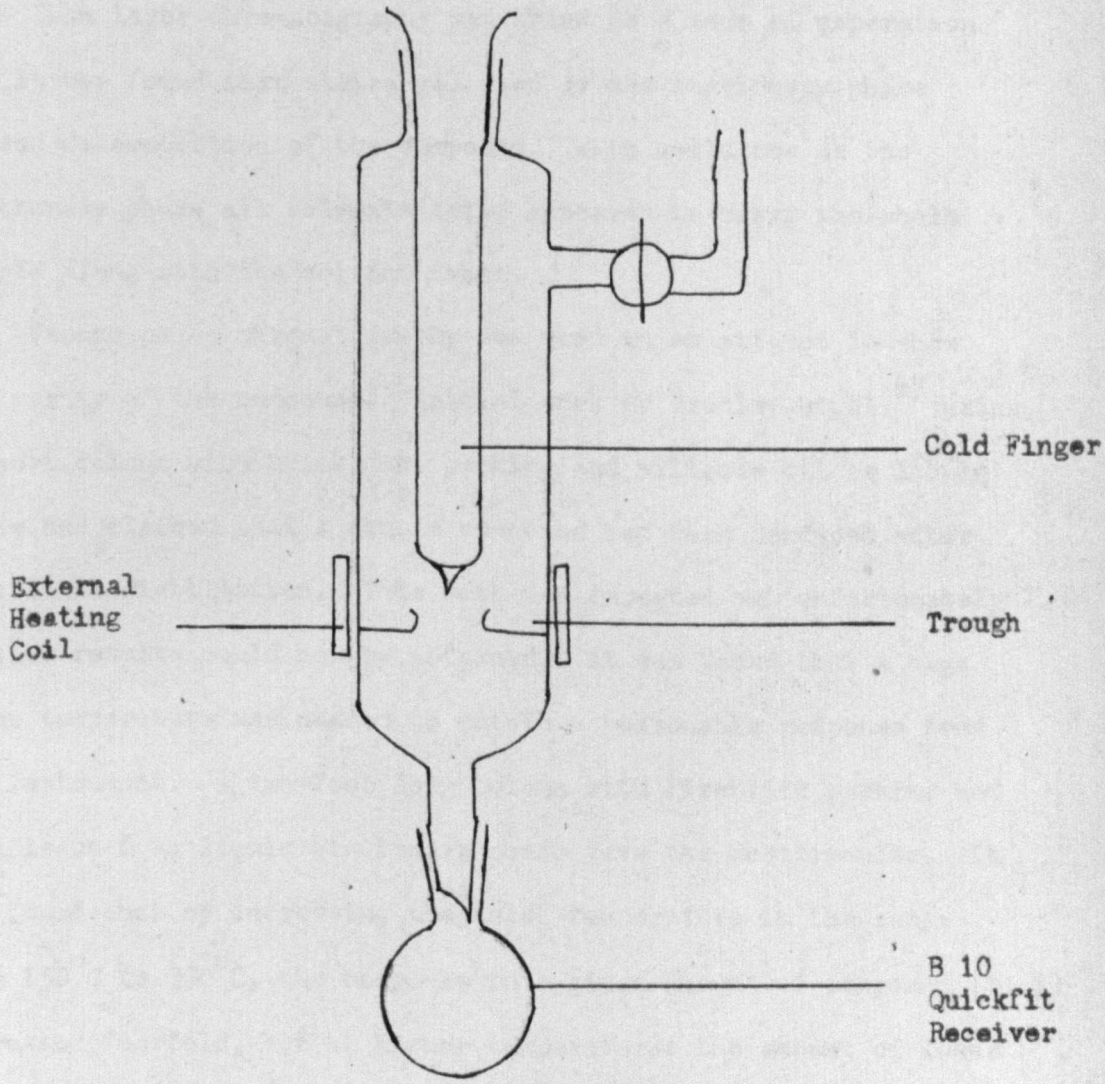
Compound A was fractionally distilled under vacuum, the main fraction distilling at 130°C at 0.1 mm. Hg. It was found that heating for long periods at the boiling point caused some decomposition. Thus attempted purification on a spinning band column was largely unsuccessful.

Purification of Compound A

A molecular distillation technique using a high vacuum and a low temperature was used to minimize any decomposition. The apparatus shown in Fig. 3 was used. The liquid was placed in the inner trough and heat applied by a heating coil around the outside of the apparatus.

Fig.3.

Molecular Distillation Apparatus



The compound was collected upon a cold finger and when sufficient had condensed it was allowed to drop into the receiver. At a pressure of $<10^{-4}$ m.m. Hg an external temperature of about 50-60°C was sufficient to slowly distil the compound.

Thin layer chromatography was tried as a mode of seperation but it was found that silica gel used as the stationary phase caused decomposition of the compound. With cellulose as the stationary phase all solvents tried appeared to carry the whole sample along with the solvent front.

Vapour phase chromatography was used in an attempt to show the purity of the compound. Initial work by Bradley et.al.[47] using a short column with brick dust packing and silicone oil as liquid phase had claimed that a single compound had been produced after fractional distillation. This work was repeated but unfortunately similar results could not be obtained. It was found that a high inlet temperature was needed to obtain a reasonable response from the instrument. A two-foot long column with Firebrick packing and 3% Apiezon L as liquid stationary phase gave the best results. It was found that by increasing the inlet temperature in the range from 150°C to 330°C, the response to a given amount of compound (1µl) increased fourfold, but at higher temperatures the amount of lower boiling constituents also increased. The best results were obtained with the column at a temperature of 330°C and an inlet temperature of 270°C. This showed that there was one main compound and some lower boiling impurities 10% of the main constituent. There was no constituent with a higher boiling point than the main constituent.

Analysis of Compound A

The analyses were carried out as previously described and a series of results gave:-

Co, 17.24% (±0.25); N, 16.28% (±0.17); C, 57.42% (±0.17); H, 9.21% (±0.09). These results are consisent with a cobalt: nitrogen: carbon ratio of 1:4:16 and a hydrogen ratio of ~30.

Molecular weight determination carried out in cyclohexane and benzene gave 332±10 and 340 ± 10 respectively. Ebullioscopic results in benzene gave erratic and lower results at approximately 310±25.

A mass spectrum shown in Fig. 4 gave a parent ion m/e 337.181858 but the most intense peak was m/e199. The parent ion is consistent with the formulation $CoC_{16}N_4H_{30}$. Calc. for $CoN_4C_{16}H_{30}$; Co,17.47; N,16.61; C,56.96%, H,8.96%.

Physical Properties of compound A

The I.R.Spectral data of this compound as the pure liquid and in carbon tetrachloride solution are given in Table 3.

The U.V.,visible and near I.R. spectrum in ethanol are shown in Fig. 5. The band positions, extinction coefficients and oscillator strengths in ethanol and cyclohexane are shown in Tables 4 and 5 respectively. The band position and extinction coefficients of the highest energy band varies considerably with the solvent used. Thus in pyridine cyclohexane and n-hexane the position is 28,800 cm^{-1} with a distinct shoulder at 34,500 cm^{-1}. Using chloroform as solvent, shifts this band to 29,800 cm^{-1} with the shoulder still at 34,500 cm^{-1}. Absolute ethanol initially gives the very broad band shown in Fig. 5 but on standing in an inert atmosphere, changes as shown in Figs 6 (a), and (b) to the band at 32,300 cm^{-1} with an extinction coefficient of

Fig 4

Compound A (Sample 1)

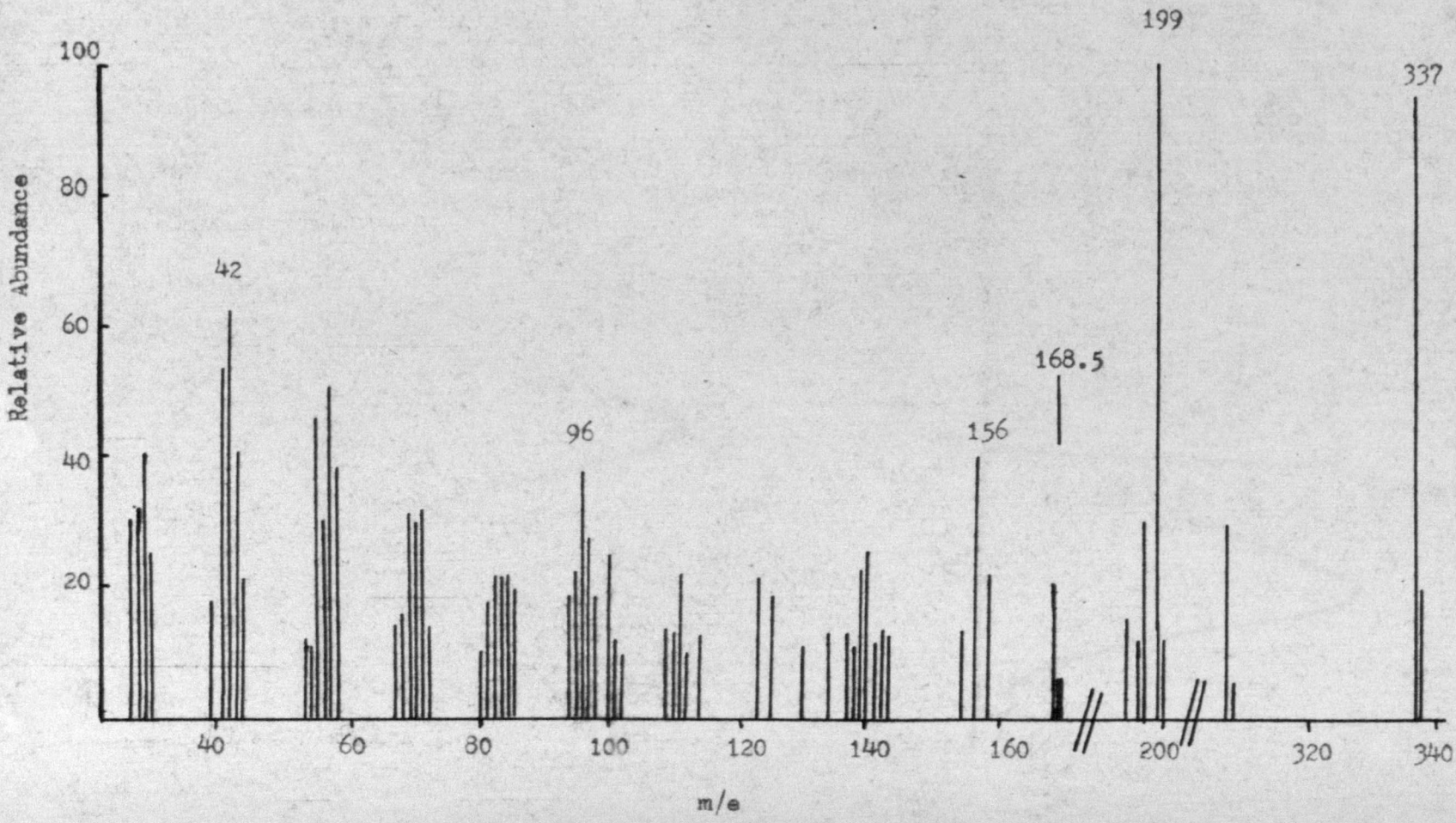
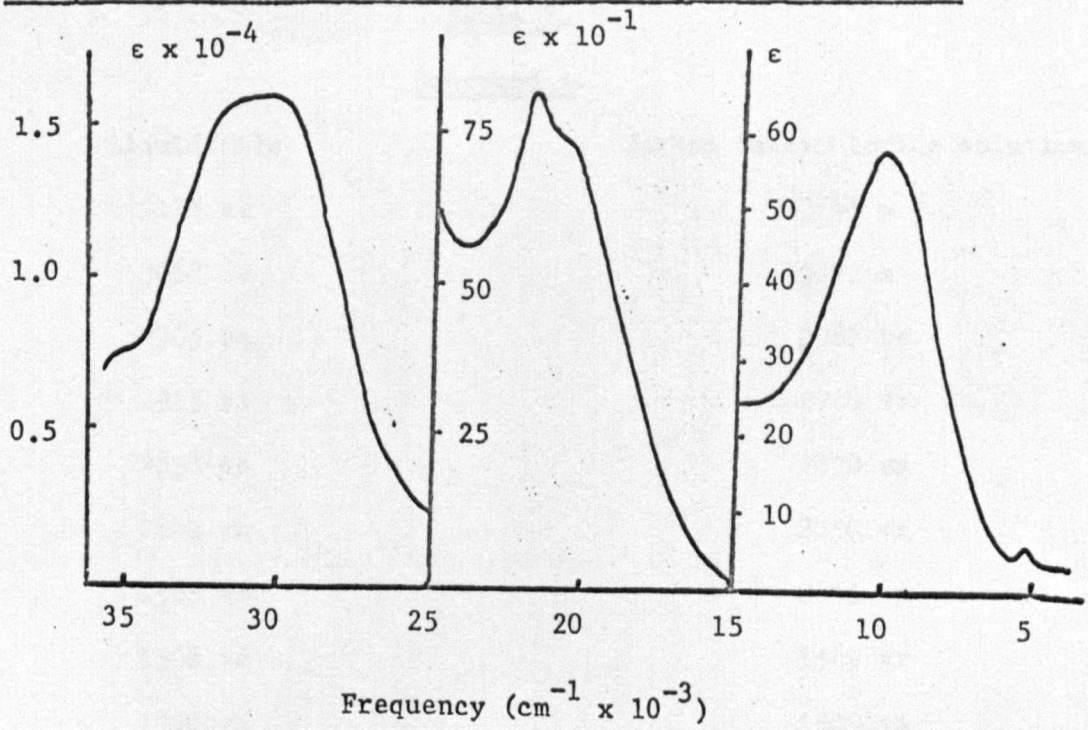


Fig.5

U.V., visible and near I.R spectrum of compound A in ethanol.



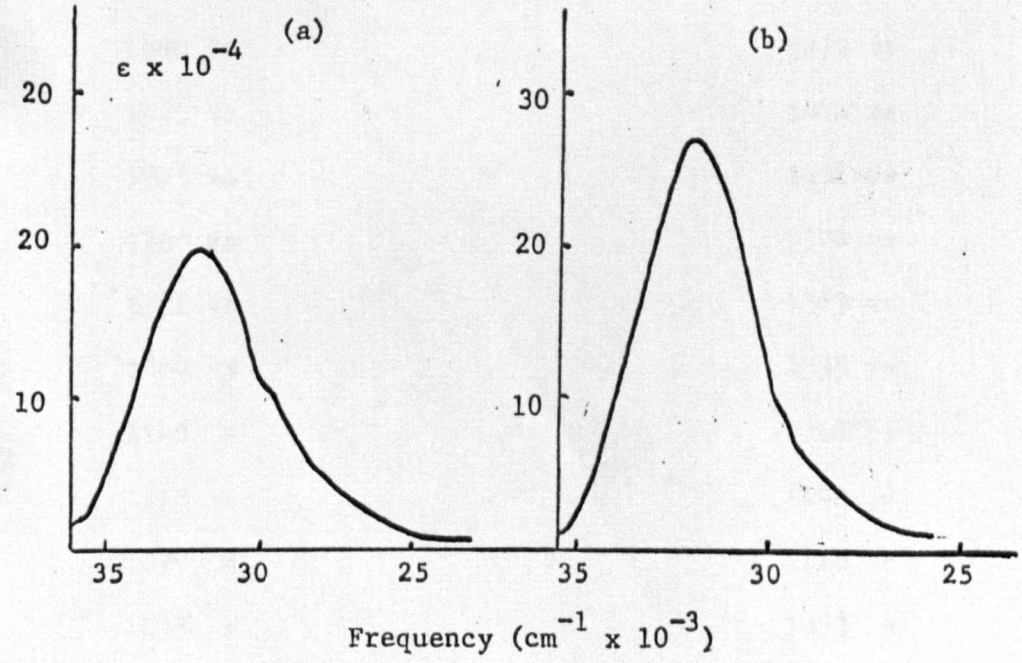


Fig. 6

Changes of the spectrum in ethanol with time.

Table 3.

Compound A.

Liquid film	Carbon tetrachloride solution.
3125 vw	3145 m
3062 w	3072 m
2965 vs	2966 vs
2915 vs	2928 vs
2858 vs	2870 vs
2642 vw	2850 vs
1565 vs	2665 m
1508 vs	1569 vs
1490 vs	1509 vs
1478 vs	1492 vs
1440 vs	1479 vs
1425 vs	1444 vs
1373 vs	1431 vs
1360 vs	1374 vs
1331 vs	1363 vs
1264 s	1335 vs
1140 s	1268 s
1112 s	1142 s
1079 m	1116 s
1043 s	1083 s
1019 m	1045 s
999 m	1021 m
951 w	1003 m
839 w	950 m

Cont.....

Cont....

Compound A.

Liquid film		Carbon tetrachloride solution.	
783	w	924	w
725	s	842	w
612	m	724	s
500	m	613	m
450	m	490	m
		455	m

Table 4

λ_{max} (cm^{-1})	ε_{max}	f
29,850	16,000	5.3×10^{-1}
22,050	795	1.2×10^{-2}
9,800	57	1.0×10^{-3}
5,900	4.3	2.77×10^{-6}

Table 5

λ_{max} (cm^{-1})	ε_{max}	f
34,500	16,700	-
28,800	27,900	6.2×10^{-1}
22,050	935	1.5×10^{-2}
10,000	35	0.94×10^{-3}

27,600 and no shoulder at 34,500 cm^{-1}. Methyl alcohol gives a similar spectrum immediately on dissolution of the cobalt compound. The extinction coefficient is in this case a little higher at 35,000. The free ligand and ligand hydrochloride give similar spectra (see later).

There is very little change in the other band positions with changing solvents as shown in Table 6.

Table 6

Solvent	$\lambda_{max}(cm^{-1})$
n-hexane	22,050 (ν_3)
n-hexane	10,000 (ν_2)
chloroform	22,050 (ν_3)
chloroform	9,760 (ν_2)
chloroform	5,800 (ν_1)
methyl alcohol	22,050 (ν_3)
methyl alcohol	9,800 (ν_2)
pyridine	22,070 (ν_3)
pyridine	9,850 (ν_2)

The spectrum of the pure liquid between glass plates was also taken and this gave band positions of 22,150 cm^{-1} (ν_3) and 10,000 cm^{-1}. A spectrum of the pure compound at liquid nitrogen temperature was taken using the apparatus shown in Fig.7. This was carried out by placing a small sample of the compound in the bottom of the container and allowing sublimation to take place at room temperature. These spectra are shown in Fig.8. The lower temperature did not change the positions of the bands but sharpened them and increased the definition of the shoulders

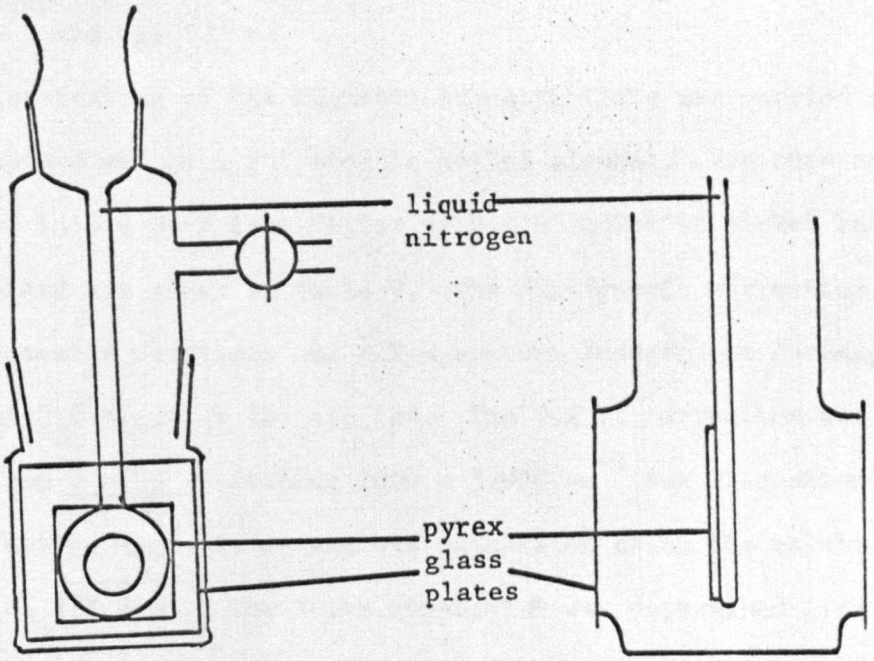


Fig. 7

Apparatus for low temperature visible spectra.

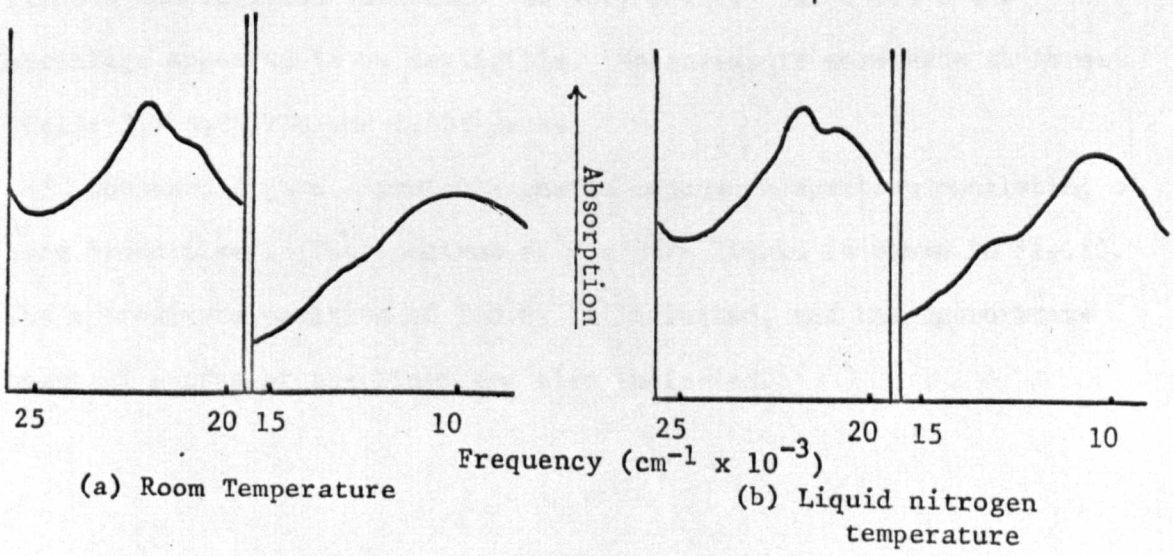


Fig. 8

Spectra of compound A (pure liquid).

at 20,900 cm^{-1} and 12,500 cm^{-1}.

The determination of the magnetic susceptibility was carried out on the pure compound and on a solution in methyl alcohol. The pure compound was distilled into a Gouy tube fitted with a B5 quickfit socket and the results obtained are shown in Table 7. The diamagnetic correction was made using Pascal's Constants and a Temperature Independent Paramagnetic correction of 350 c.g.s. x 10^{6} applied. The T.I.P. correction was calculated from $\frac{8 k^{2} N \beta^{2}}{10Dq}$ assuming 10Dq = 5.900 cm^{-1} (see discussion).

The effective magnetic moment was calculated using the relationship $\mu_{eff} = 2.83 \sqrt{X_m (T + \theta)}$. The Weiss constant θ was determined from the graph of X_m^{-1} against T shown in Fig.9. The measured results at lower temperatures than room temperature were adjusted for shrinkage of the liquid. It was found that between 223°K and 193°K the liquid was very viscous and apparent shrinkage was very small. Below 193°K the shrinkage appeared to be negligible. Measurements were made at three fields 3,785, 5,750 and 6,675 gauss.

Compound A gave a proton magnetic resonance spectrum consisting of very broad lines. The spectrum of the pure liquid is shown in Fig.10. The approximate position of T.M.S. is indicated, and the approximate chemical shifts of the lines are also indicated.

Table 7.

T	χ_g	χ_m	χ_m^1	$1/\chi_m^1$	μ_{eff} B.M.
298	21.81	7,350	7,180	1.393	4.14
273	23.78	8,015	7,845	1.277	4.16
253	25.00	8,425	8,305	1.206	4.13
223	28.01	9,440	9,270	1.079	4.11
193	32.71	11,025	10,855	0.921	4.13
153	40.86	13,770	13,600	0.735	4.13
133	46.72	14,745	15,575	0.649	4.13
113	54.94	18,515	18,345	0.548	4.15
				Average	4.13 ± 0.015.
		Methyl alcohol solution			
298	22.15	7,420	7,250	-	4.16

χ_g = gram. susceptibility (c.g.s. x 10^6)

χ_m = molar susceptibility (c.g.s. x 10^6)

χ_m^1 = corrected molar susceptibility (c.g.s. x 10^6)

μ_{eff} = observed magnetic moment.

Fig 9.

The temperature dependence of Magnetic Susceptibility

of compound A

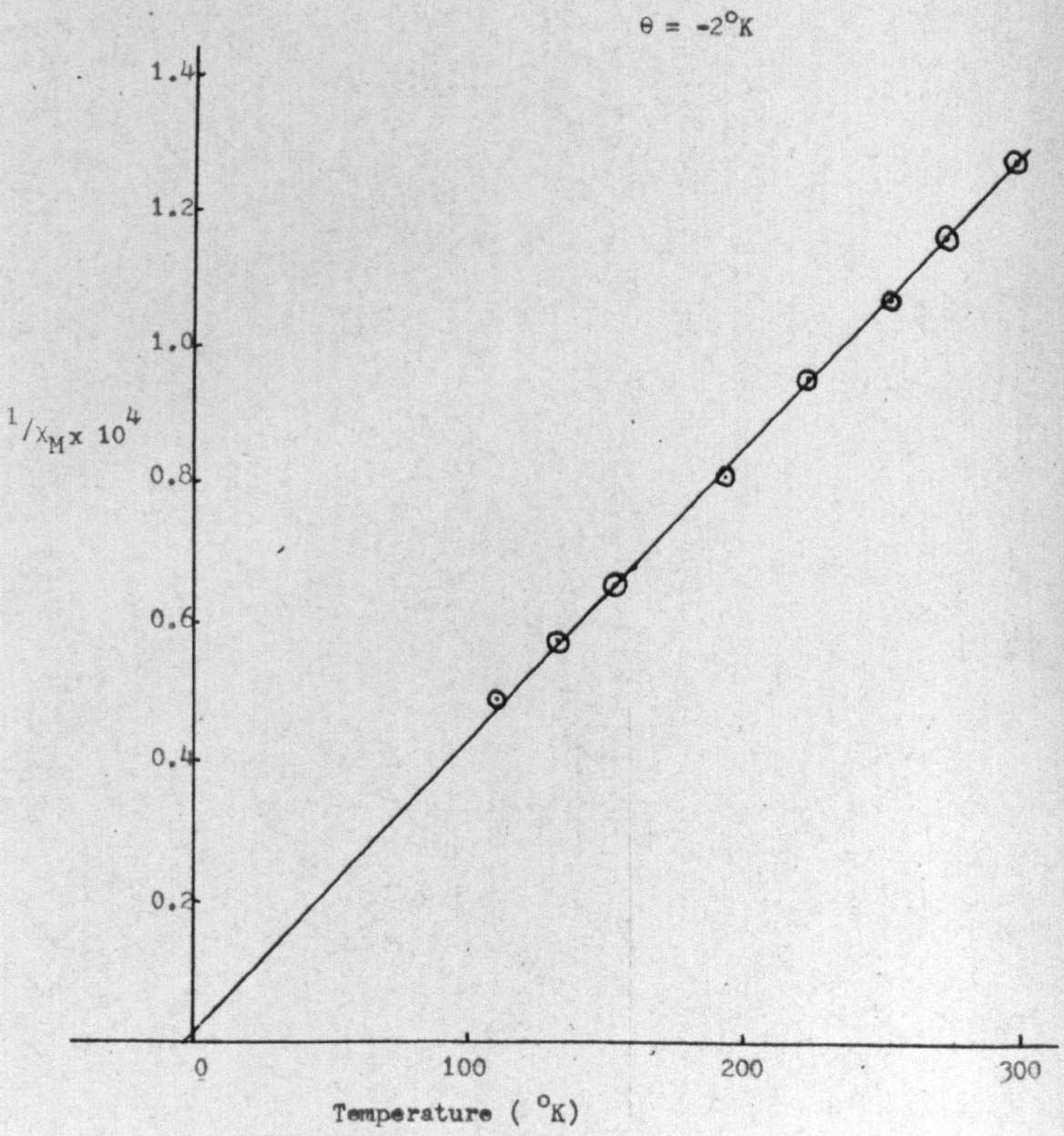
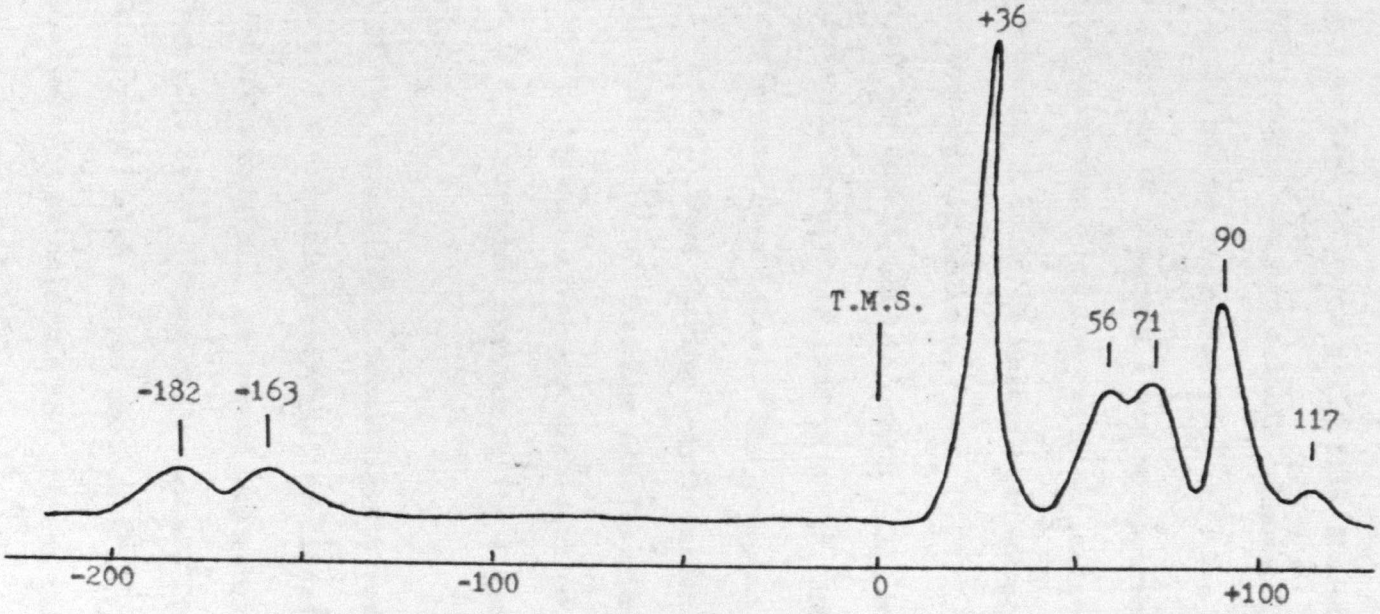


Fig 10.

N.M.R. spectrum of compound A



General chemical properties of Compound A

Compound A was stable if stored under vacuum or nitrogen in the dark. If the compound was exposed to air a solid film formed on the surface of the liquid. This solid was not soluble in non-polar solvents and compound A could not be recovered from it. The passage of dry oxygen through a solution of compound A had no apparent effect as the compound A could be recovered from the resultant solution. A hydrocarbon solution of compound A could be shaken with water and the compound A recovered from the organic solvent.

Attempted oxidation of the cobalt (II) to cobalt (III) with H_2O_2 generally succeeded in producing involatile gums with I.R. and U.V. spectra similar to the free ligand (see later). The compound showed a marked susceptibility to acids. Thus shaking a hydrocarbon solution with a $^{N}/_{1000}$ hydrochloric acid or $^{M}/_{100}$ disodium ethylenediamine tetra-acetic acid solution the organic layer was decolourized and the aqueous layer gave an U.V. absorption similar to the ligand hydrochloride (see later).

Attempted reduction of the cobalt (II) to cobalt (I) with sodium borohydride in the presence of a possible co-ordinating ligand e.g. triphenyl phosphine, proved unsuccessful. Attempted oxidation of the cobalt using a redox system e.g. Fe^{III} (dipyridyl)$_3$ $\longrightarrow$ Fe^{II}(dipyridyl)$_3$ in the presence of excess dipyridyl also proved unsuccessful. Compound A was shown to react with aluminium trichloride and silicon tetrachloride but the aluminium and silicon compounds produced were involatile and could not be purified.

The extraction of cobalt from compound A

Two methods were successfully used to remove cobalt from compound A, in order to isolate the organic ligand. These were an anion exchange method and precipitation of cobalt as the benzimidazole complex.

Ion exchange method

Compound A was dissolved in 8N hydrochloric acid and this solution passed through a Dowex 1-X-8 anion exchange column. This column had been pre-treated with 8N hydrochloric acid. The cobalt was retained at the top of the column as the bright blue chloro- complex $(CoCl_4)^{2-}$. A yellow solution was obtained from the column. This strong acid solution was evaporated under vacuum to give a bright yellow very viscous oil. This was dried under high vacuum and gave the following analysis.

C 44.48% H, 9.36% N 13.28% Cl 23.88% Total 91.02%

The unaccounted 8.98% was assumed to be oxygen possibly present as water. The analysis corresponded to $N_4C_{16}H_{32}(HCl)_3(H_2O)_{1.6}$. This is in good agreement with Bradley et.al.[47] who found $N_4C_{16}H_{33}(HCl)_3(H_2O)_{1.2}$ from analysis. Molecular weights were attempted (osmometrically in chloroform) but erratic results were obtained.

This compound (the ligand hydrochloride) was soluble in water, alcohols, chloroform and methylene dichloride. The I.R. frequencies are given in Table 8. The U.V. and visible spectrum showed only one very intense absorption at 32,500 cm^{-1} with no change in frequency position with change of solvent (e.g. water, methanol, chloroform or methylene dichloride). As the molecular weight and purity of the ligand hydrochloride were uncertain no accurate extinction coefficient could be obtained but it was very high of the order of 35,000 to 40,000

Table 8

Ligand Hydrochloride Thin film (cm^{-1})	Ligand Thin film (cm^{-1})
3220 vs	3250 vs
3040 vs	3040 vs
2960 - 2830 vs	2980 vs
2700 s	1640 vs
2590 m	1590 vs
2500 m	1475 s
2050 w	1460 s
1692 m	1390 s
1640 vs	1360 vs
1590 vs	1340 vs
1460 s	1310 vs
1445 s	1275 vs
1380 s	1255 vs
1350 s	1132 s
1300 vs	1100 m
1268 vs	1072 w
1252 vs	1040 w
1130 s	1020 m
1098 s	835 m
1068 s	795 m
1035 m	750 s
1015 s	
835 m	
788 s	
745 s	
658 m	

The N.M.R. spectra taken in deuterium oxide and deuterochloroform are shown in Fig 11. (a) and (b) respectively. The triplet, singlet, quartet and single broad absorption in deuterium oxide were in the ratio 6:3:4:1. In deuterochloroform, coupling the bands at 9.95 ppm and 9.64 ppm together, the ratio of the absorptions was 6:3:4:1:1:1.5.

The spectrum at - 12°C was taken and this increased the definition of the bands at 9.95, 9.64 ppm and 5.10 ppm. The N.M.R. spectrum became diffuse if the ligand hydrochloride was stored. The ligand hydrochloride could not be purified by sublimation (it decomposed when heated under vacuum) but a mass spectrum was obtained (Fig 12.). This showed the highest ion to be $^{m}/_{e}$ 149 and a more intense ion at $^{m}/_{e}$ 140.

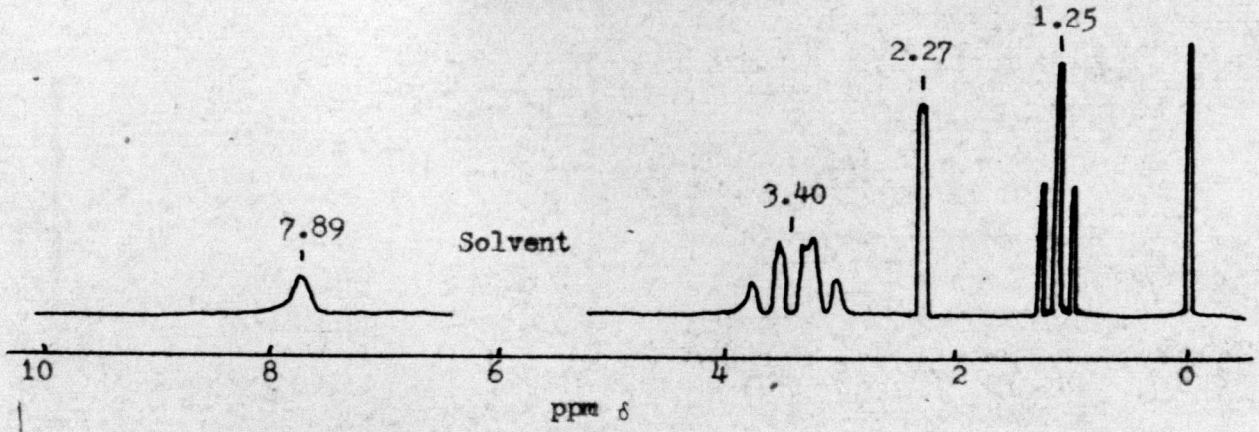
Cobalt benzimidazole precipitation

Benzimidazole forms an insoluble complex with cobalt (II). Thus treatment of compound A in chloroform or ethanolic solution caused precipitation of the cobalt benzimidazole complex. In solution there was some compound A, (precipitation over long periods was allowed to take place but there always remained some unreacted compound A), the ligand and excess benzimidazole. Seperation of these constituents using ethanol as solvent was found difficult and so the method in which chloroform was used as solvent will be described.

Compound A was dissolved in chloroform and to this solution was added a solution of benzimidazole in chloroform. This benzimidazole solution contained a slight excess of benzimidazole needed to precipitate all the cobalt. The solution was kept in the dark for several hours to ensure full precipitation of the benzimidazole complex. The

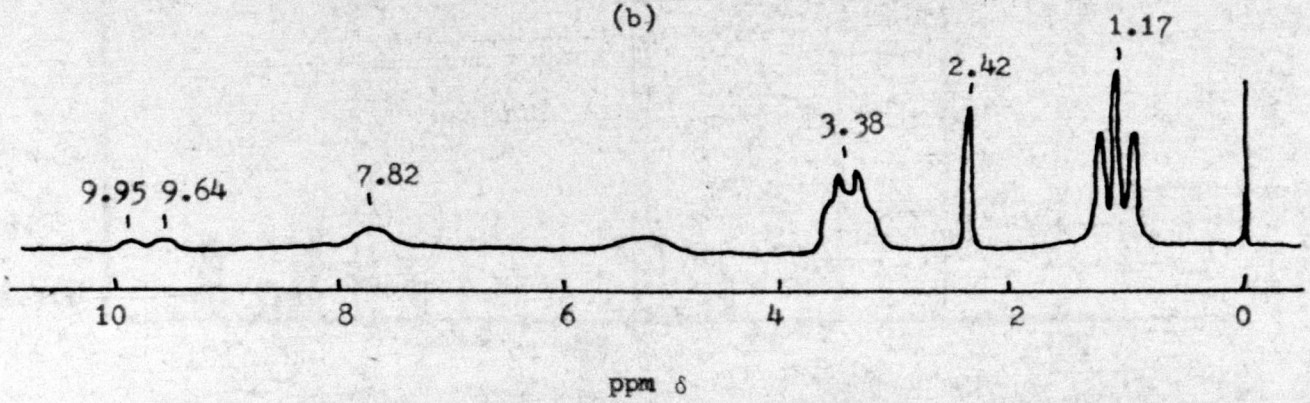
Fig 11.

(a)



N.M.R. spectrum of the ligand hydrochloride in deuterium oxide.

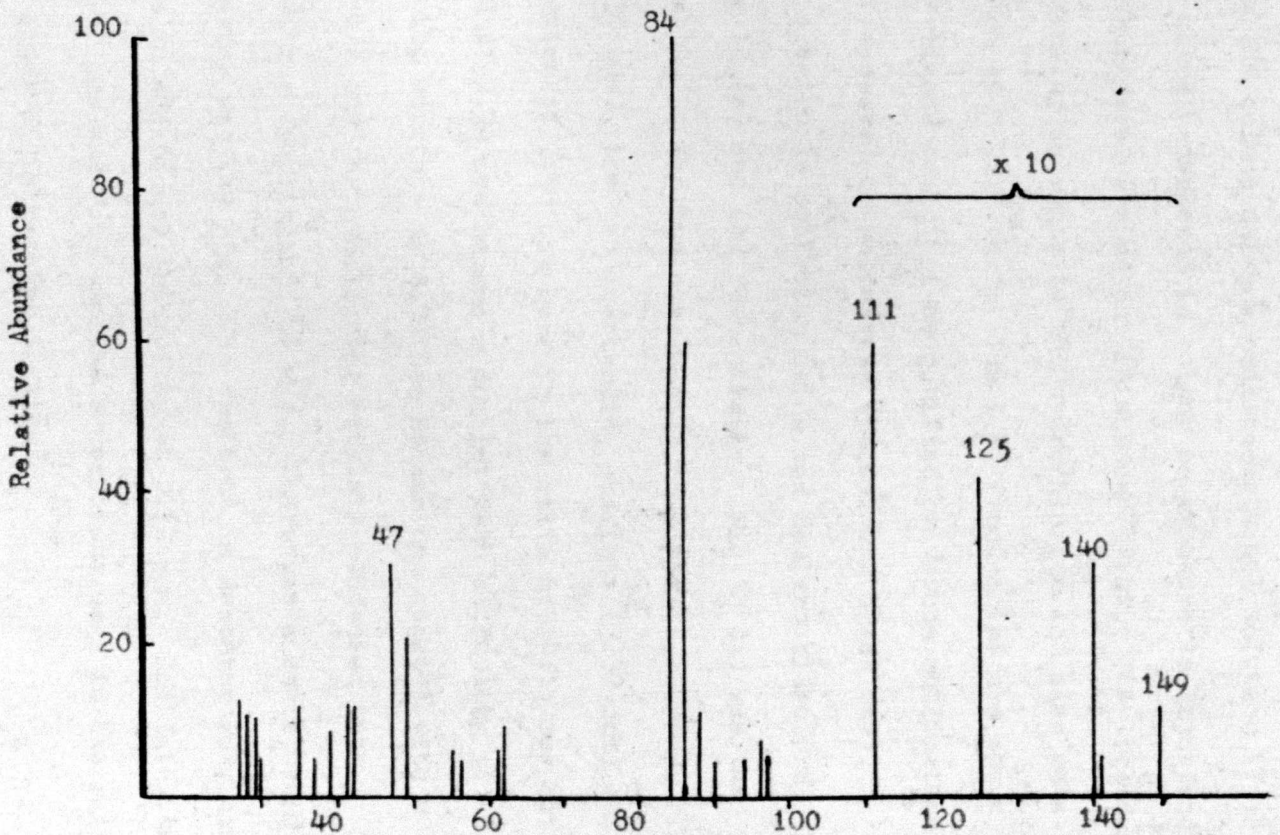
(b)



N.M.R. spectrum of the ligand hydrochloride in deuterochloroform.

Fig 12.

Ligand Hydrochloride



solution was filtered and passed down an active alumina column, this removed residual compound A. The benzimidazole was removed from the column by washing with a benzene-methanol solution (95:5). The ligand was removed from the column using a benzene-methanol solution (75:25).

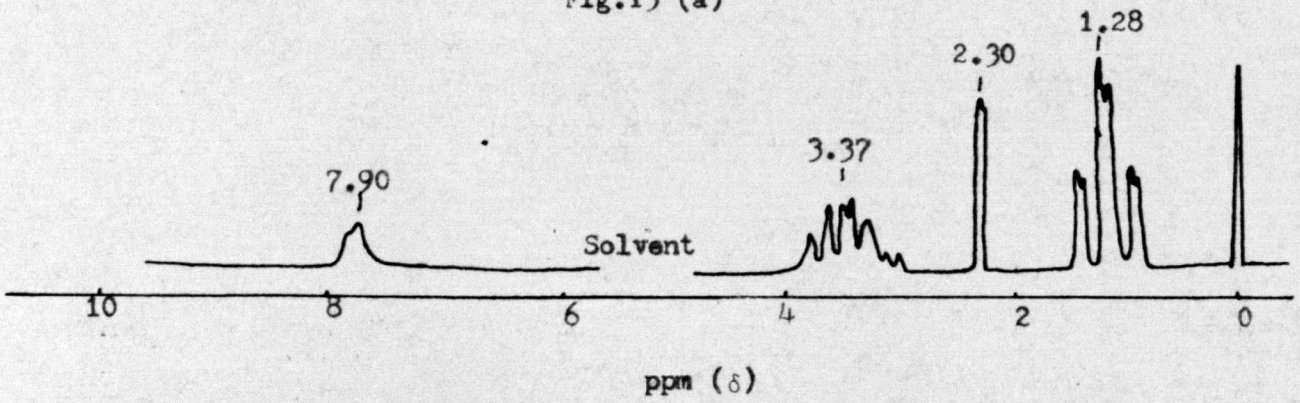
The ligand quickly darkened in colour on exposure to light and so above operations were carried out in subdued light. The ligand was soluble in similar solvents to the hydrochloride and also gave an U.V. absorption at 32,500 cm^{-1}. The I.R. frequencies are shown in Table 8. The ligand could not be purified by vacuum sublimation as on heating it appeared to polymerize (becoming a black tar).

The N.M.R. spectra in deuterium oxide and deuterochloroform are shown in Fig 13 (a) and (b) respectively. Fig 13 (a) was the spectrum taken at 40°C, the two overlapping triplets (1.28 ppm), the singlet (2.30 ppm), the two overlapping quartets (3.37 ppm) and the broad absorption at 7.90 ppm were in the ratio 6:3:4:1: respectively. At 10°C the band at 7.90 ppm became a doublet with a coupling of ~6 c/s. The two overlapping quartets at 3.37 ppm became one quartet with a coupling of 7.4 c/s and the overlapping triplets condensed into a single triplet with a coupling of 7.4 c/s. There was a small broad absorption appearing at 5.49 ppm. The spectrum in deuterochloroform was similar with an additional absorption at 9.12 ppm. Combining the absorption at 7.96 ppm and 7.69 ppm the absorptions were in the ratio 6:3:4:1:1:1 (in order of increasing δ value).

Deuteration of Compound A

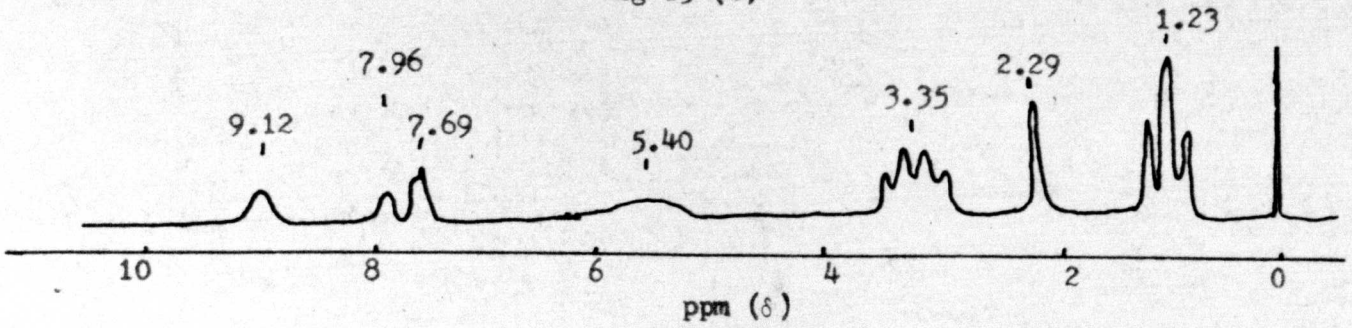
The cobalt compound was dissolved in deuterochloroform and this solution shaken in the absence of light under nitrogen, with deuterium

Fig.13 (a)



The N.M.R. spectrum of the ligand in deuterium oxide.

Fig 13 (b)



The N.M.R. spectrum of the ligand in deuterochloroform.

oxide. The deuterium oxide was removed and fresh deuterium oxide added and shaken again. The deuterochloroform solution was seperated and the solvent removed under vacuum. The cobalt compound produced was distilled under high vacuum. The U.V. and visible spectra of the resulting compound were similar to the original compound but the I.R. spectrum showed some definite changes. The I.R. spectrum is given in Table 9, and the differences in the I.R. spectrum from the original compound shown in Fig 14. A mass spectrum Fig 15. gave ions at m/e 337, m/e 338, m/e 339, m/e 340, m/e 341 and m/e 342.

Deuteration of the ligand hydrochloride

The ligand hydrochloride was obtained from the anion exchange procedure. It was dried under high vacuum then dissolved in deuterium oxide. After some time the deuterium oxide was removed and replaced by fresh deuterium oxide. This procedure was repeated several times. The I.R. frequencies are given in Table 9. The N.M.R. spectrum of the deuterated ligand hydrochloride in deuterochloroform was very similar to Fig. 11 (b) except for the absence of the bands at 5.10 ppm, 9.64 ppm and 9.95 ppm. The absorption at 7.82 ppm was much sharper but still very broad (~16c/s at half peak height).

Hydrogenation of Compound A

Lithium aluminium hydride

Compound A was shaken with lithium aluminium hydride in ether solution for several hours. The lithium aluminium hydride was destroyed and the ether solution removed and evaporated. The remaining compound was distilled and found to be the original compound A in 80% yield.

Table 9

Deuterated compounds

Compound A	Ligand Hydrochloride
Liquid film (cm^{-1})	Thin film (cm^{-1})
3125 w	3220 w
2960 vs	3040 w
2915 vs	2990 s
2855 vs	2950 w
2642 vw	2460 m (sh)
1565 vs	2320 s
1489 vs	1622 vs
1465 vs	1580 vs
1422 vs	1475 s
1368 vs	1460 s
1352 vs	1420 s
1330 vs	1395 s
1264 s	1360 s
1211 w	1300 s
1126 m	1274 s
1112 m	1150 m
1099 m	1117 s
1085 m	1090 m
1061 m	1005 m
1042 w	972 m
1020 w	880 vw
1000 w	800 w
946 w	700 m

Cont.....

Cont.....

Compound A	Ligand Hydrochloride
Liquid film (cm^{-1})	Thin film (cm^{-1})
837 w	595 w
778 w	555 m
725 w	
617 m	
545 m	

Fig 14

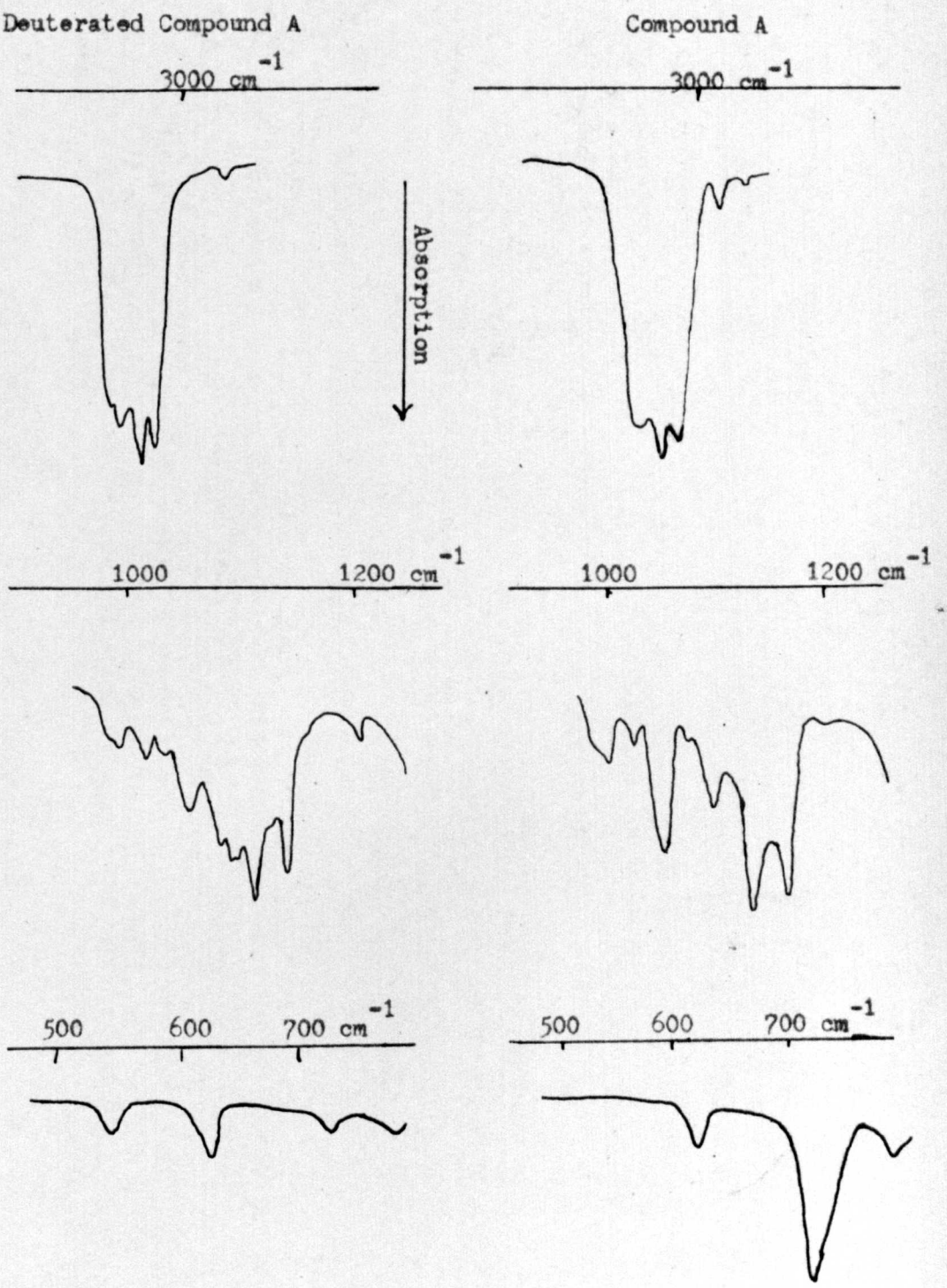
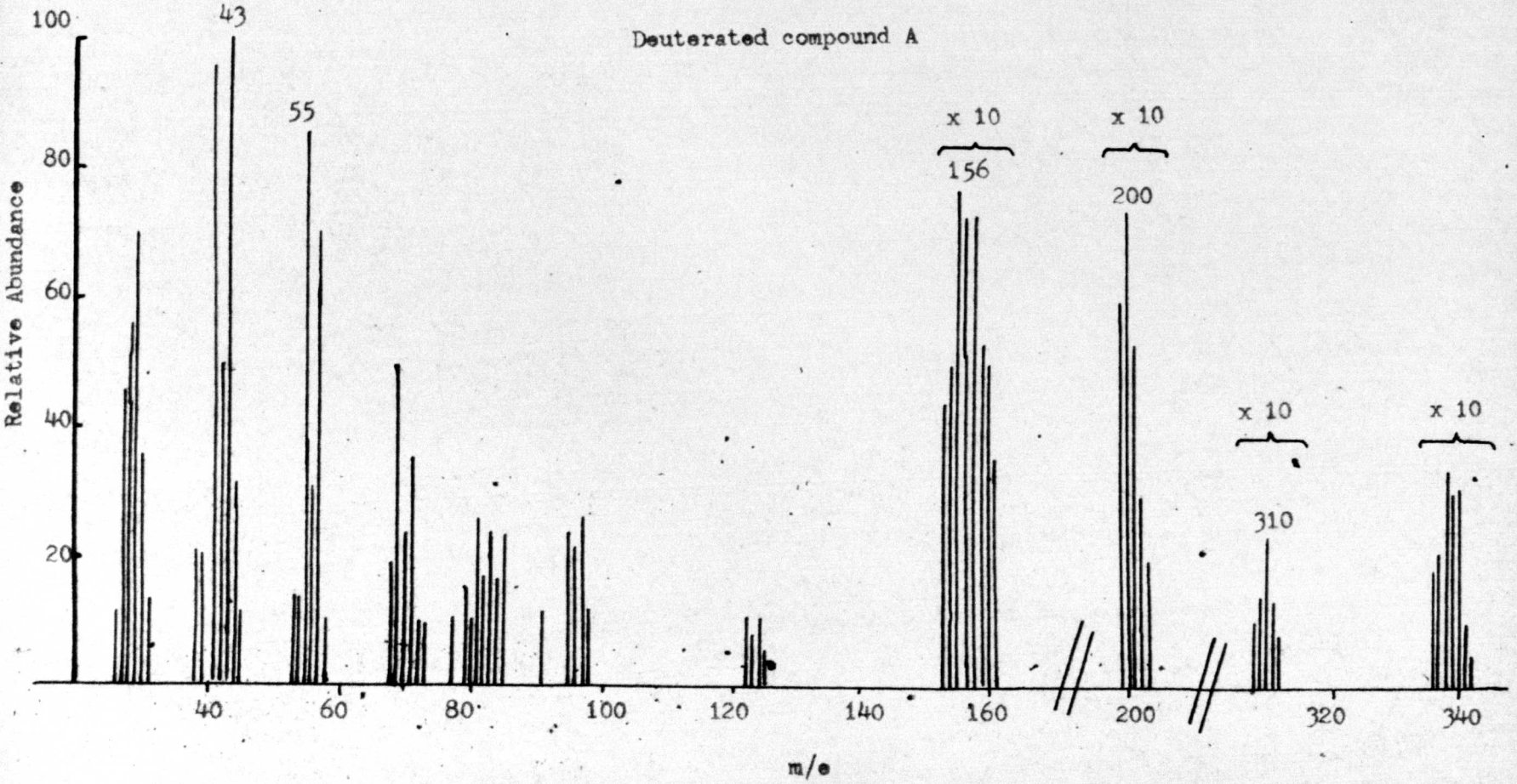

Deuterated Compound A
Compound A
3000 cm-1
3000 cm-1
Absorption
1000
1200 cm-1
1000
1200 cm-1
500
600
700 cm-1
500
600
700 cm-1

Fig 15.

Deuterated compound A



Hydrogenation at High Temperature and Pressure

Compound A (2.2g.) was taken and dissolved in methanol (50 ml). This solution was placed in a hydrogenation bomb. Hydrated platinum oxide (approx. 20 mg.) was added to the solution and then the bomb filled with hydrogen at 100 atmosphere. The bomb was then heated to 160°C for six hours. After cooling and releasing the hydrogen atmosphere the solution was filtered. The resulting solution was shown to contain no cobalt. The solution was evaporated to small volume by removing methanol and weighed. This solution was then shown by V.P.C. to contain three compounds and excess methanol. Integration with a Kent Integrator was used to find the amounts of these constituents. The smallest constituent was 10% of the total. The other constituents X and Y were 42% and 48% respectively. The total weight of the products were shown to be 1.44 g. Samples of X and Y were collected from the V.P.C. and examined.

X was shown by I.R. to be unsaturated, giving a strong absorption at 1670 cm^{-1}. This is possibly and unconjugated imine. A strong peak was also present at 3300 cm^{-1} possibly due to N-H stretch of a secondary amine.

The I.R. spectrum of Y showed it to be a simple secondary amine.

The analysis shown below and the N.M.R. spectrum were consistant with this compound being 1:3 bisethylaminobutane.

Found: C, 66.21; N, 1954; H, 13.48%

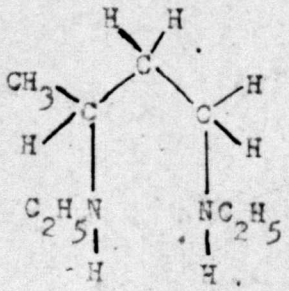
Calc. for $C_8N_2H_{20}$, C, 66.59; N, 19.44; H, 13.97%

$$n_D^{24} \quad 1.443_8$$

1:3 bisethylaminobutane was prepared by a slight modification

of the method of Robinson and Olin[50]. Crotonalkehyde was slowly added to an aqueous methanolic solution of ethylamine at 0°C. This was placed in a hydrogenation bomb and Raney nickel added. The mixture was hydrogenated at 175°C for 5 hours with a hydrogen pressure of approximately 150 atmosphere. The resulting mixture was distilled and the fraction boiling at 140°C taken. A small portion purified by V.P.C. gave identical infrared and N.M.R. spectra to the hydrogenation product (Y).

Thus the main product of the hydrogenation of the cobalt compound was:-



The total yield of the hydrogenation products calculated from the amount of cobalt compound less the weight of cobalt was equal to 80%. Thus the yield of 1:3 bisethylaminobutane was 38.4%.

Attempted hydrogenation of the ligand and ligand hydrochloride

The ligand was prepared from the benzimidazole separation. The ligand was dissolved in methanol and shaken for 4 hours using hydrated platinum oxide as catalyst under 15 lb/sq.in. of hydrogen. The resulting solution was filtered and the methanol evaporated. The resulting product gave a similar I.R. and U.V. spectrum to the ligand.

The ligand was dissolved in methanol and heated in a bomb to 160°C

under a pressure of hydrogen of approximately 150 atom.(platinum oxide added as catalyst). A green viscous liquid was obtained on evaporation of the solution. The U.V. spectrum was very similar to the ligand and I.R. spectrum showed strong absorptions at 1675 cm^{-1} and 1600 cm^{-1}.

The ligand hydrochloride gave similar results under the same conditions.

Attempted halogenation of Compound A

Bromine

Bromine was slowly added to the cobalt compound dissolved in hexane. A dark green oil was precipitated. After the addition of excess bromine the solvent was decanted and the green oil washed with hexane. Drying this green compound under vacuum produced a sticky solid. Several preparations showed that this solid had variable cobalt and bromine contents. No way was found of purifying the product and so it was not studied further.

N-Bromosuccinimide

The method used by Gollman[51] to brominate the ketoamine complexes of chromium (III) was tried. Compound A (390 mg 1.15m.mole) was dissolved in chloroform (15 ml). To this was added a solution of N-bromosuccinimide (412 mg. 2.3 m.mole) in chloroform (10 ml). A blue solid was precipitated from the solution. The solution was filtered and the chloroform solution evaporated to dryness under vacuum. A brown gum resulted which contained only a trace of cobalt and the I.R. and U.V. spectra were very similar to the ligand. Some features of this compound indicated that it was possibly a bromination product of the ligand. The U.V. spectrum showed an intense band at 31,200 cm^{-1} whereas the ligand shows a band at 32,500 cm^{-1}. The I.R. spectrum

showed very strong absorption in the region 3,200 cm^{-1} to 2,900 cm^{-1} similar to the ligand, a medium band at 1760 cm^{-1} and a strong band 1700 cm^{-1} which are not present in the ligand. There is a band at 640 cm^{-1} which may be due to a C-Br stretching vibration.

The solvent for the initial part of the experiment was changed from chloroform to ether but a large amount of blue solid was obtained and also the brown gum was produced.

Tertiary butyl hypochlorite

Tertiary butyl hypochlorite was prepared by the reaction of chlorine on tertiary butyl alcohol in the presence of sodium hydroxide. This compound was distilled immediately prior to use.

Compound A (200 mg 0.595 m.moles) was dissolved in ether and to this solution was added tertiary butyl hypochlorite (130 mg. 1.2 m.mole). There was a green precipitate formed, the solution was filtered and the ether removed. From the residue a red oil (28.3 mg) was sublimed at 60° C(10^{-4} mm Hg pressure). A very small amount of a red solid was sublimed at 80°C (10^{-4}). The residue was a black sticky gum with an I.R. spectrum similar to the ligand. The green solid was analysed and gave the following results.

Co 16.0%; Cl, 19.3% N, 11.80%; C, 40.01%; H, 6.99%; Total 94.1%

This analysis gives the ratio of Co:Cl:N:C:H of 1:2:3:12:26. This compound was soluble in water and methanol but only slightly soluble in ethanol and insoluble in non-polar solvents. The U.V. spectrum in ethanol showed an intense band at 32,000 cm^{-1}. No other bands were found in the visible region (using methanol solution or nujol mull). The band at 32,000 in strong solutions tailed to

14,000 cm^{-1}, possibly covering any weak d-d transitions. The I.R. spectrum showed a band at 3,220 cm^{-1} probably due to N-H stretch. Strong bands at 1640 cm^{-1} and 1580 cm^{-1} were very similar to the ligand. There were two medium bands at 790 and 725 cm^{-1}.

A molecular weight determination in methanol using a Mechrolab Osmometer gave a value of 195 showing that the compound was either dissociated or impure.

The red oil appeared to decompose in a sealed tube under nitrogen but immediately after preparation it gave the I.R. spectrum shown in Table 10. The U.V. and visible spectrum was slightly different from compound A. A very intense band at 29,000 cm^{-1} with slight shoulders at 27,800 cm^{-1} and 35,000 cm^{-1} was observed using hexane as solvent. Two equally intense bands at 21,800 cm^{-1} and 20,600 cm^{-1} with a shoulder at 19,500 cm^{-1} were observed in this same solvent.

Analysis for cobalt and chlorine gave :-

Co 14.3% Cl 12.0%

Monochlorination to give a compound of molecular weight 371.5 requires a cobalt analysis of 15.9% and a chlorine analysis of 9.55%. Dichlorination to give a compound of molecular weight 406 required a cobalt analysis of 14.5% and a chlorine analysis of 17.5%. Thus it appears that this compound is possibly a mixture of mono- and dichlorinated compound A; the low cobalt analysis may be due to decomposition. A mass spectrum was taken but this showed a high intensity peak at m/e 337 and some very low intensity ion peaks at m/e 369; m/e 370; m/e 371; and m/e 372.

Table 10

Chlorinated compound A (liquid film) cm^{-1}

2970	s
2930	s
2870	s
1564	vs
1506	m
1485	s
1414	vs
1360	s
1325	vs
1263	s
1140	m
1112	s
1085	s
1050	s
1020	m
987	m
940	w
858	w
800	w
725	w
618	w
596	w

Preparation of metal compounds from the ligand and ligand hydrochloride

Cobalt

Preparation of the cobalt compound was attempted with a method used by Weber[52]. This was essentially the reaction of cobalt acetate with the ligand in ethanolic solution in the presence of a base e.g. sodium carbonate. The products of this reaction were not identified but compound A could not be obtained.

The preparation of the cobalt compound was attempted using a modified method of Holm et.al.[53].

Compound A (0.123g 0.355 m moles) was taken and the ligand hydrochloride was dried under vacuum and dissolved in ethanol (20 ml). To this was added anhydrous cobalt chloride (0.08g. 0.355 m.moles) dissolved in tetrahydrofuran. To this mixture was added an ethanolic solution of sodium ethoxide until the blue-green colouration turned brown. The solution was shaken for 4 hours and after this time the solution was filtered. The ethanol was evaporated off under vacuum and the residue extracted with pentane. This solution was evaporated to dryness and from the resulting residue was sublimed a yellow-brown liquid. This was identified by the I.R., U.V. and visible spectra as compound A. The yield of this compound was 18.4 mg (15%).

Nickel

A similar method was used: the nickel was added as the tetraethylammonium tetrabromonickelate (II). A brown liquid which distilled at 50°C (10^{-4} mm Hg), was produced. The I.R spectrum is shown in Table 11.

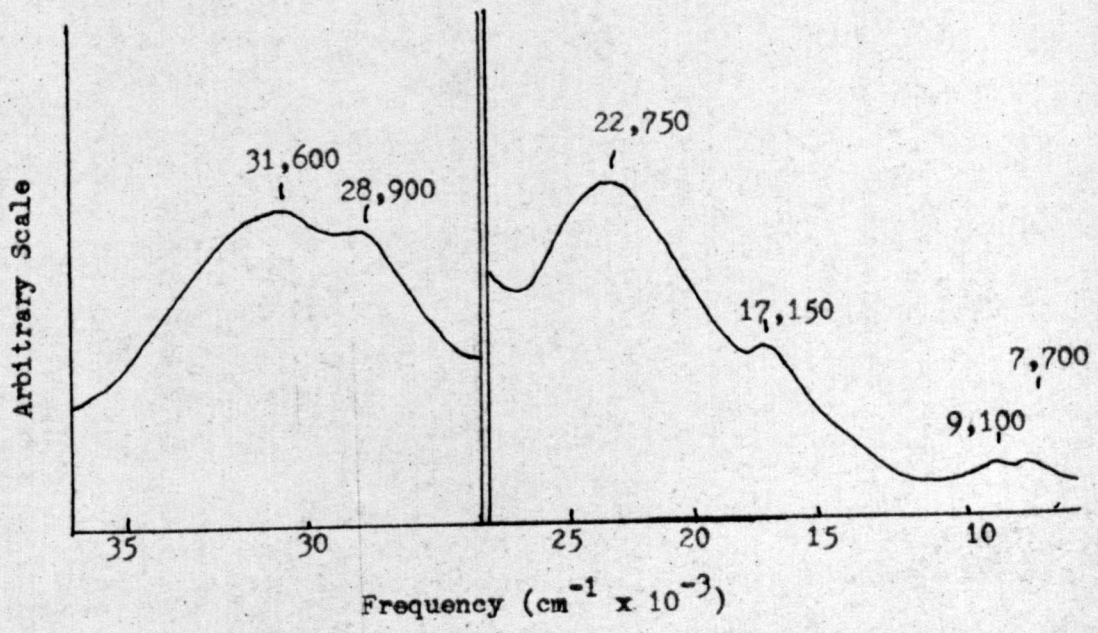
The U.V. and visible spectra were taken using cyclohexane and ethanol as solvents and are shown in Fig 16 (a) and (b) respectively.

Table 11.

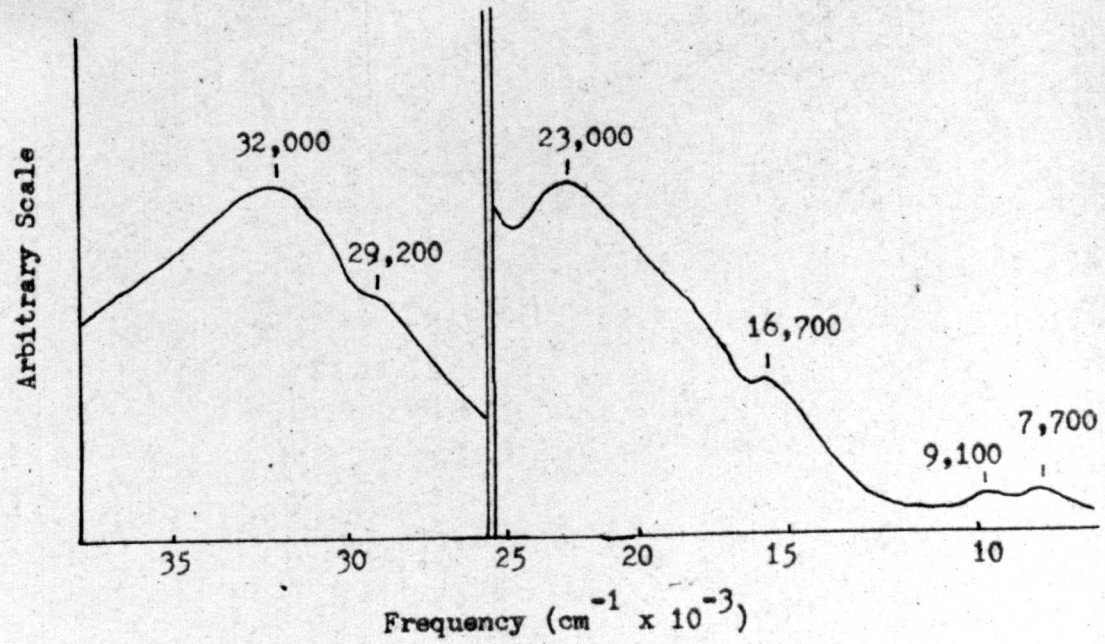
Nickel analogue pure liquid	Zinc analogue pure liquid
3090 w	3075 w
3000 m (sh)	3000 m (sh)
2970 vs	2970 vs
2930 vs	2930 vs
2900 vs	2875 vs
2880 vs	2860 s
1580 vs	1585 vs
1520 vs	1500 vs
1495 vs	1490 vs
1435 vs	1440 vs
1360 s	1425 vs
1335 vs	1372 vs
1263 s	1330 vs
1140 m	1259 s
1114 s	1147 s
1040 s	1120 s
1018 m	1082 m
802 m	1046 s
725 s	1020 m
615 m	1000 w
515 s (broad)	840 w
450 m	783 m
	720 s
	612 m

Fig.16.

(a)



(b)



U.V. and visible spectra of the nickel analogue of compound A

The yield of the compound in several preparations was ~10%. The compound was analysed for nickel only.

A mass spectrum Fig 17. gave a molecular ion for the ligand with Ni^{58} of m/e 336.

Found	Ni, 17.2%
Calc. for $NiN_2C_{16}H_{30}$	Ni, 17.39%

Zinc

A slightly different method was used for zinc as the above method appeared to be unsuccessful. The ligand was produced by reacting compound A with benzimidazole. The solution was filtered and to the filtrate was added a solution of anhydrous zinc chloride in ethanol. A slight excess of zinc chloride being added because some was precipitated as the zinc benzimidazole complex. The solution was again filtered and then sodium ethoxide in ethanolic solution added. This was shaken for 4 hours and then filtered. The ethanol was removed under reduced pressure. From the residue a pale yellow liquid was distilled at 60°C (at 10^{-4} mm Hg pressure). The compound had the I.R. spectrum shown in Table 11. The U.V. spectrum taken in cyclohexane showed two bands at 27,800 cm^{-1} (~15,000) and 29,000 cm^{-1} (~16,500). The N.M.R. spectrum in carbon tetrachloride solution is shown in Fig 18. The coupling of the doublets at 6.89 ppm and 3.91 ppm was 8.0 c/s. The coupling of the five line system centred at 3.21 ppm was 7.2 c/s. No coupling could be assigned to the system centred at 1.05 ppm as the lines were slightly unsymmetrical.

The ratio of the N.M.R. bands was 8:3:4:1:1. in order of increasing δ value. The spectrum in deuterochloroform was very similar but on shaking this solution in an N.M.R. tube with

Fig.17

Nickel analogue of compound A

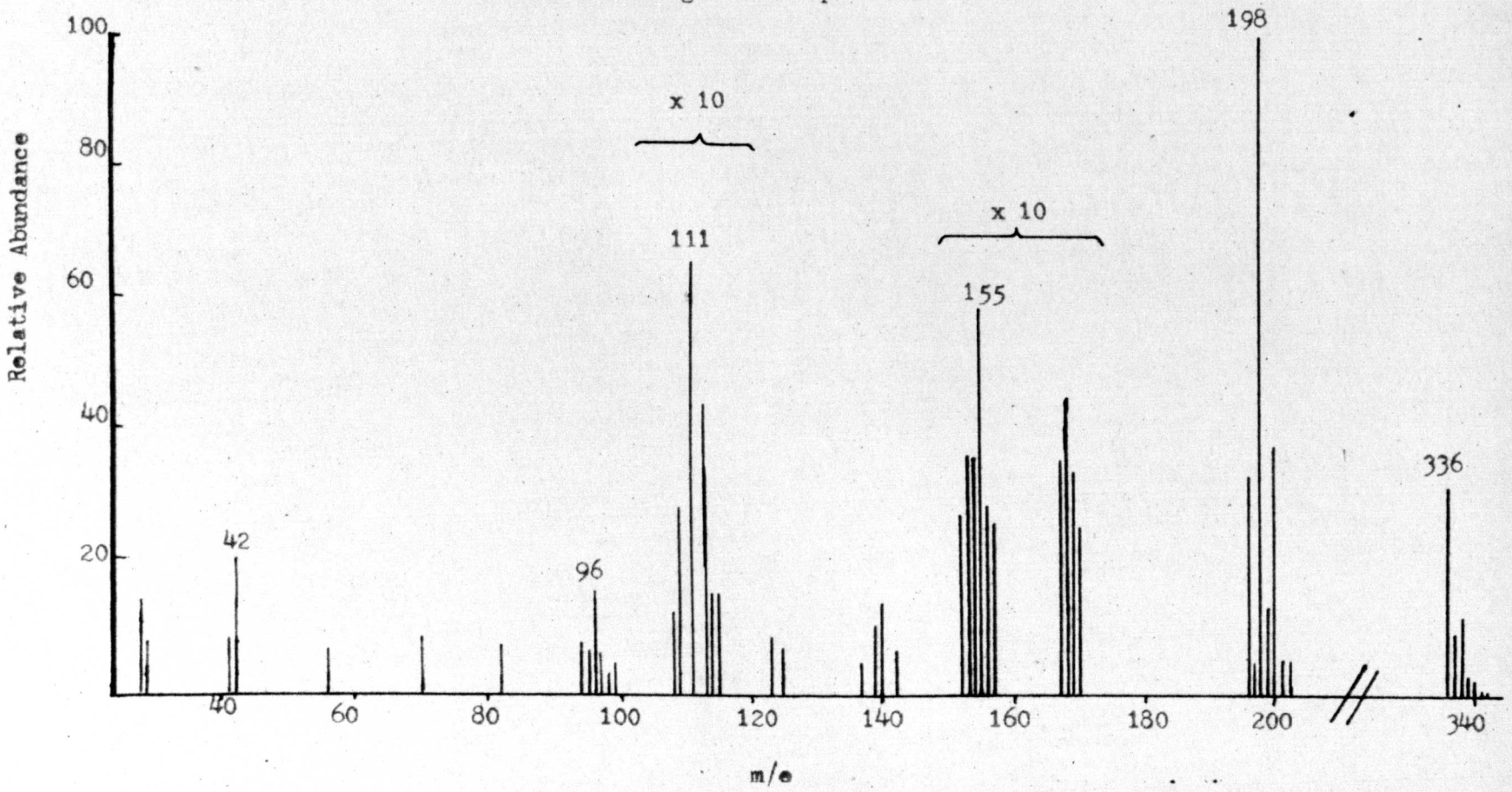
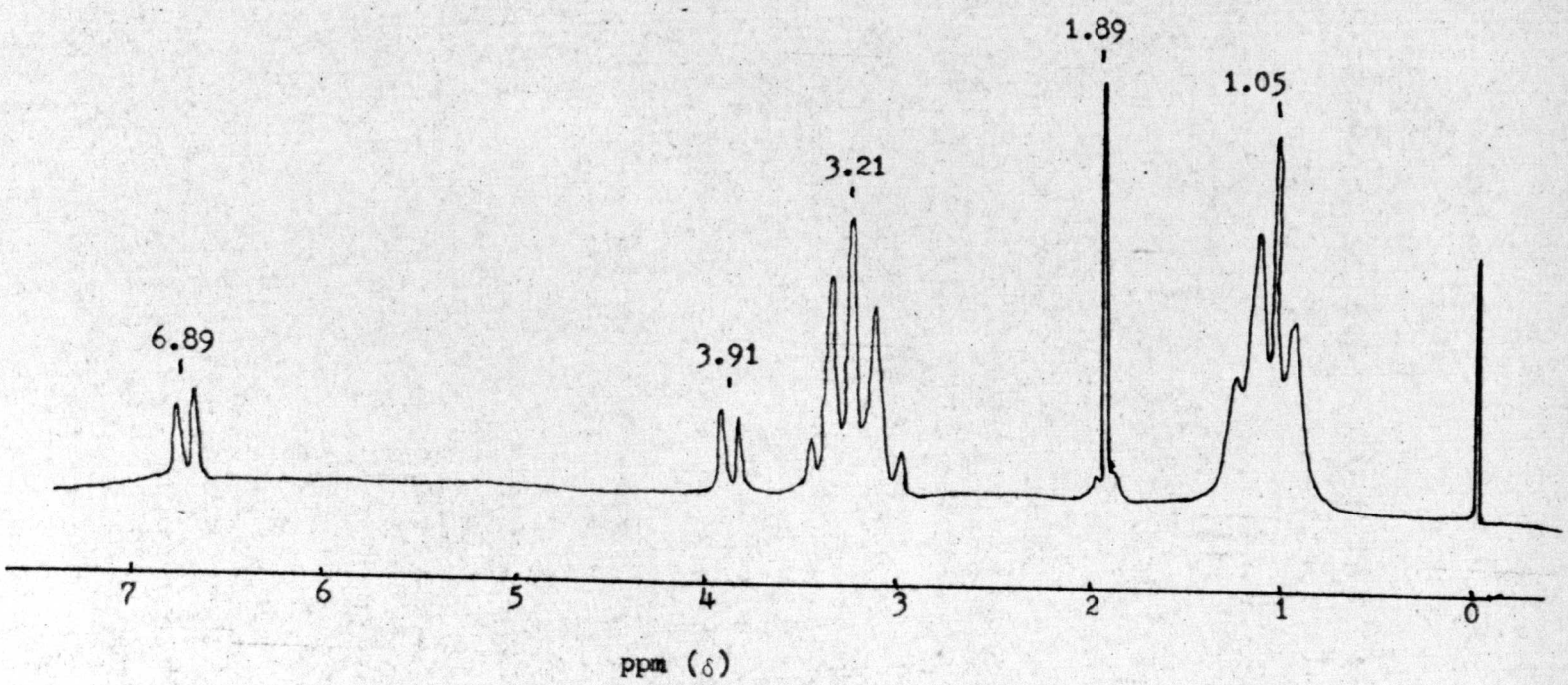


Fig 18.



N.M.R. spectrum of the zinc analogue of compound A

deuterium oxide the doublet centred at 4.04 ppm slowly disappeared and the doublet at 7.00 ppm became a singlet at 7.01 ppm. The five line spectrum at 3.21 ppm also changed slightly.

A mass spectrum Fig.19. showed the presence of the original compound A (m/e 337), it also showed possible molecular ions containing the ligand with Zn^{64}, Zn^{66}, Zn^{67} and Zn^{68} at m/e 342; m/e 344; m/e 345; and m/e 346 respectively.

Bis-hexamethyldisilylamino cobalt (II)

This compound was prepared by a slight modification of the method used by Wannagat[37]. Lithium hexamethyldisilylamide was prepared by reaction of n-butyllithium with hexamethyldisilylazane

Anhydrous cobalt bromide (5.38 g.; 24.6 m.moles) dissolved in tetrahydrofuran (50 ml) was added very slowly to lithium hexamethyldisilylamide (8.20g.; 49.2 m.moles). After addition of the cobalt bromide solution the solution was refluxed for two hours and then all the solvent removed under vacuum. The resultant mixture was extracted with pentane giving a green solution. This was filtered then evaporated to small volume (causing a solid to crystallize out of solution). This solution was filtered. The solid was distilled at 100°C (0.1 mm Hg pressure). The filtrate was treated with carbon tetrachloride and re-evaporated to low volume and filtered. The crystals produced were distilled at 100°C (0.1 mm Hg pressure).

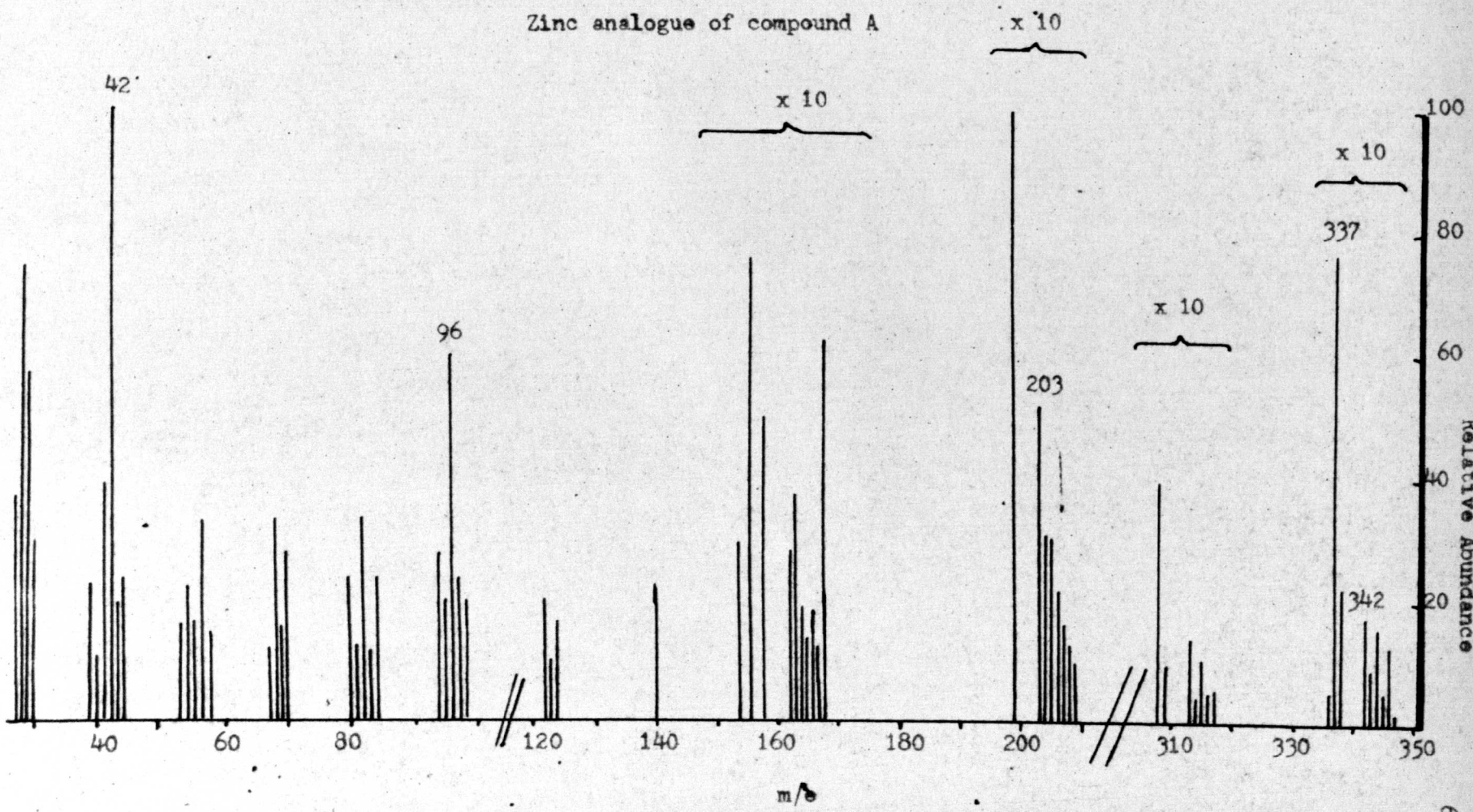
Yield 5.4 g (58%).

The compound was distilled into thin walled glass ampoules which were sealed under vacuum. These bulbs were used for analyses and other measurements described later.

The compound produced was analysed for cobalt and nitrogen

Fig 19.

Zinc analogue of compound A



by the methods described in the first part of this section. Weighed glass ampoules were broken and the glass remaining filtered off and weighed.

Found. Co,15.35; N,7.44; Br, 0.1;Li, 0.1%

Calc for $CoN_2Si_4C_{12}H_{36}$; Co,15.52; N,7.38%

Physical Properties

Some of the compound was distilled into a fine pyrex tube which was sealed under vacuum. This gave a melting point of 72°C. The I.R. spectrum was taken in solution by breaking an ampoule into degassed dry carbon tetrachloride. Nujol mulls were unsuccessful as almost invariably on making them up the compound was oxidized. The I.R. spectrum is shown in Table 12.

The U.V. and visible spectra were taken in pentane and the spectrum is shown in Fig. 20. The band positions and extinction coefficients are shown in Table 13. The extinction coefficients possibly have a large margin of error as very dilute solutions were used.

The molecular weight was determined cryoscopically in cyclohexane. This gave a value of 362 (required for a monomer 379).

The magnetic susceptibility was determined by distillation of the compound directly into a Gouy tube. The susceptibility was also determined in methylcyclohexane solution. The results are shown in Table 14. and the graph of χ_m^{-1} against T (giving a Weiss constant $\theta = 0°K$) is shown in Fig.21.

Table 12

Bis-hexamethyldisilylamino cobalt (II).

Carbon tetrachloride solution (cm^{-1})

2955 vs

2900 vs

1258 vs

1247 vs

1182 w

1060 w

1032 s

998 - 80 Broad vs

922 s

855 - 35 Broad vs

(800 - 750) CCl_4

710 m

672 s

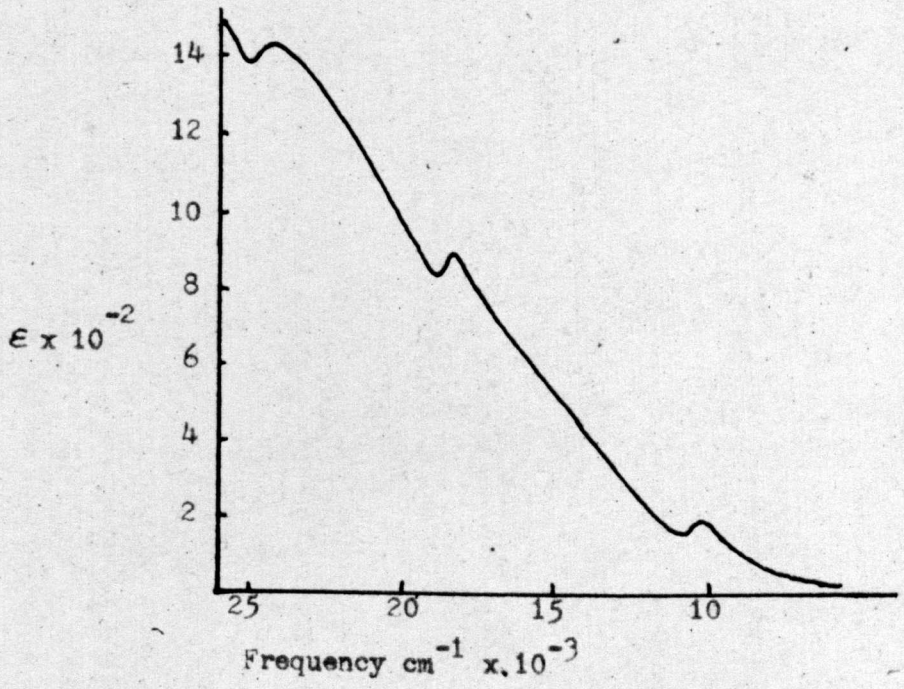
639 m

615 m

580 w

475 m

Fig 20.



Visible and near I.R. spectrum of bis-hexamethyldisilylamino cobalt (II)

Table 13.

λ_{max} (cm^{-1})	ε_{max}
10,650	180
17,100	845
24,400	1,430

Table 14

T(°K)	χ_g	χ_m	χ_m^1	$\mu_{eff.}$ (B.M.)
298	25.15	9,520	9,800	4.84
273	27.40	10,400	10,280	4.84
253	29.45	11,180	11,460	4.82
233	32.10	12,180	12,460	4.82
213	35.25	13,320	13,600	4.82
173	43.70	16,580	16,860	4.84
133	57.70	21,850	22,130	4.85
			Average	4.83 ± 0.015
Methylcyclohexane solution				
298°	28.60	10,840	11,120	5.1

χ_g = gram. susceptibility (c.g.s. x 10^6)

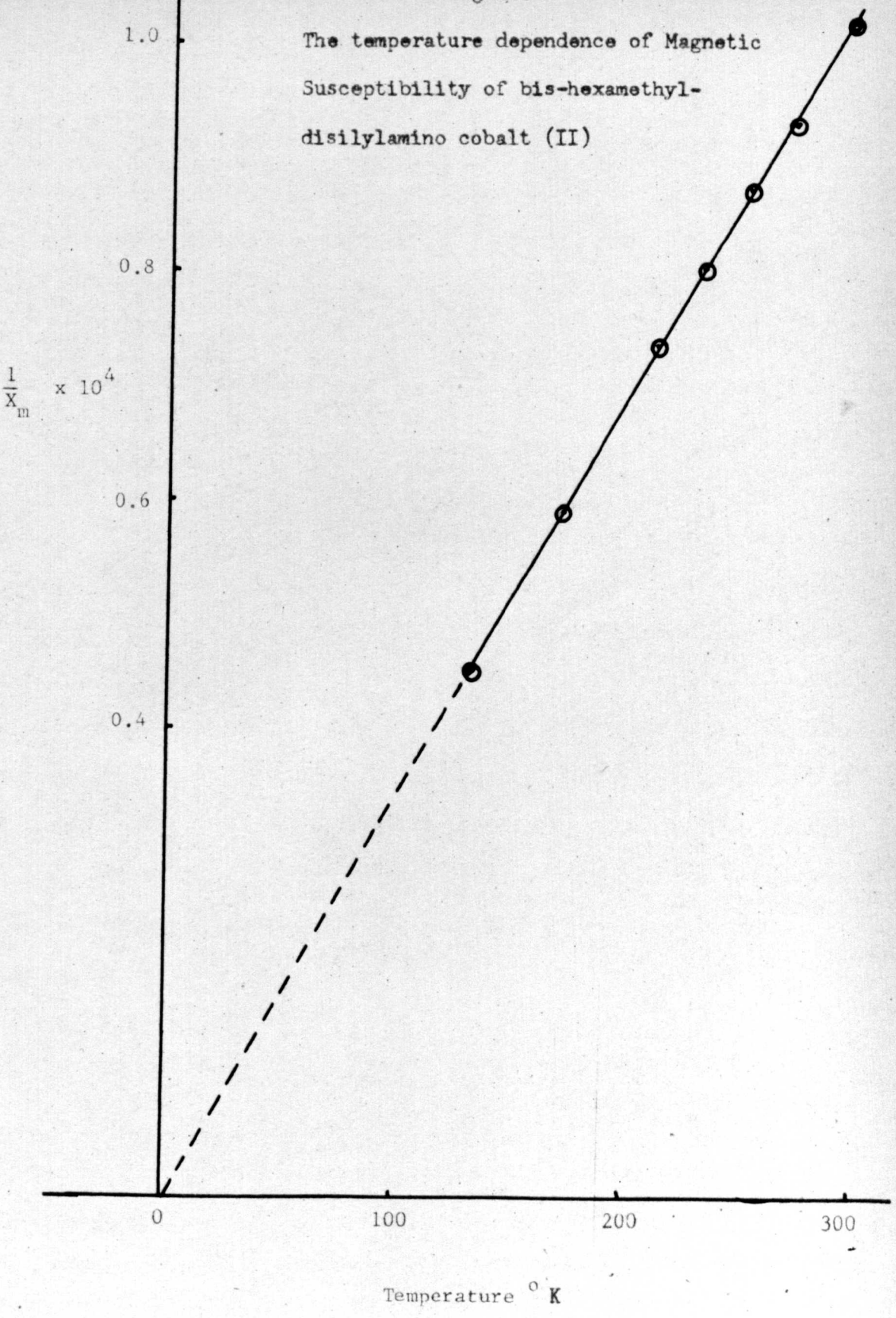
χ_m = molar susceptibility (c.g.s. x 10^6)

χ_m^1 = corrected molar susceptibility (c.g.s. x 10^6)

μ_{eff} = effective magnetic moment.

Fig 21.

The temperature dependence of Magnetic Susceptibility of bis-hexamethyl-disilylamino cobalt (II)



Reaction with alcohols (tertiary butanol and triethylcarbinol)

The compound was freshly distilled into a flask and dissolved in degassed benzene. To this was added excess alcohol and the solution refluxed. The solution immediately turned purple. The solution was concentrated by evaporation under vacuum (The solvent removed was shown by V.P.C. to contain hexamethyldisilazane). The solutions were filtered and the insoluble alkoxides washed with fresh benzene. The solids were dried under vacuum and gave the following analyses.

$Co(OCEt_3)_2$	Co 20.2% (found)	20.4% (required)
$Co(OCMe_3)_2$	Co 28.6% (found)	28.8% (required)

The I.R. spectra are given in Table 15. and the U.V. and visible spectra taken as nujol mulls are shown in Fig.22. with frequencies given in Table 16.

Both solids were rather sticky and packing into a Gouy tube was not attempted. The triethylcarbinolate was very soluble in tetrahydrofuran and magnetic susceptibility measurements were carried out in this solvent (The U.V. and visible spectrum of the tetrahydrofuran solution was very similar to the nujol mull spectrum). The magnetic results were as follows:-

T	χ_g	χ_M	χ_M^1	μ_{eff}
298	36.4	10,510	10,700	5.04

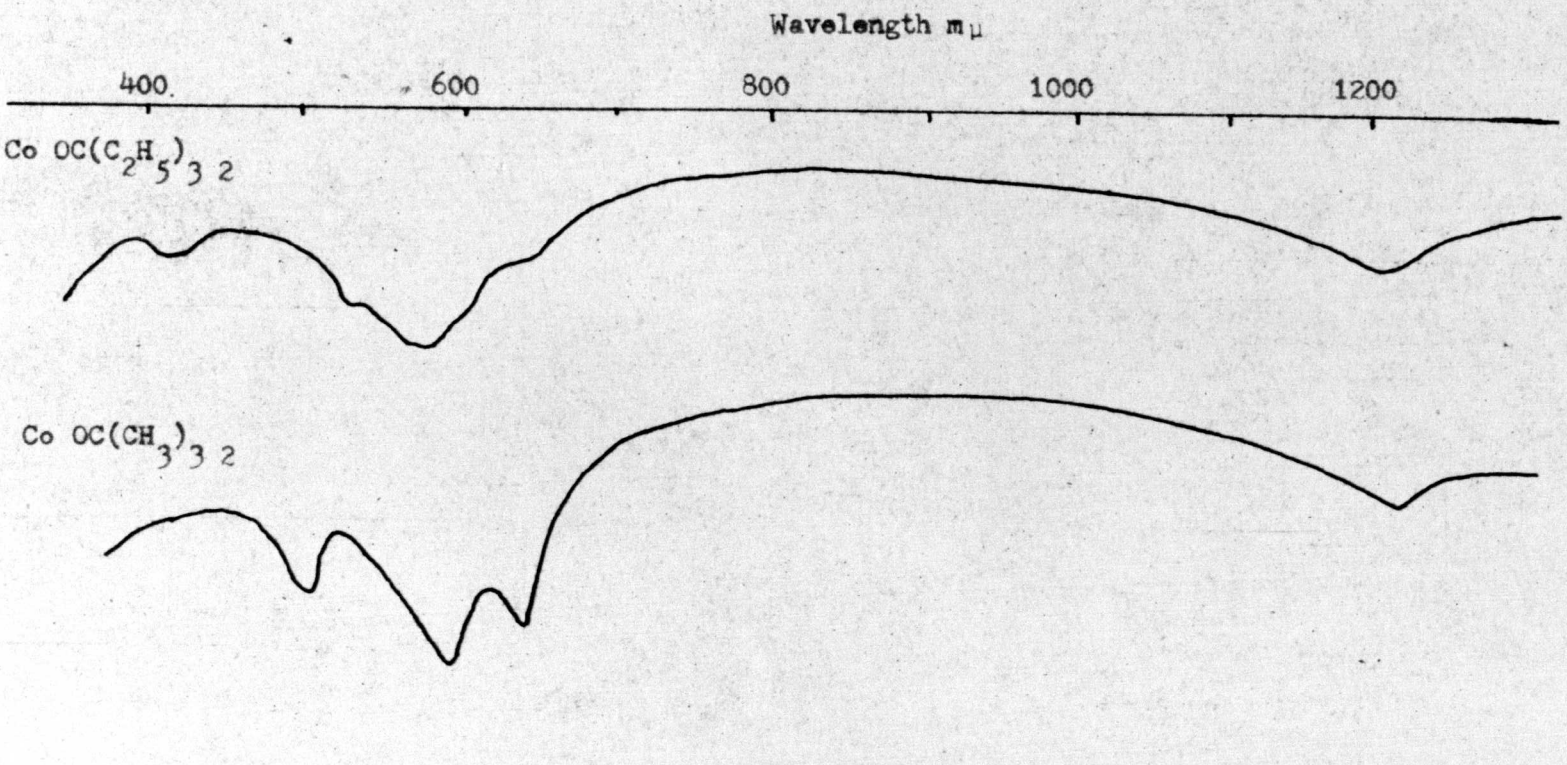
The reaction of other lithium dialkylamides with cobalt halides.

The lithium dialkylamides were prepared as described previously for lithium diethylamide. Several amines were used including $-NMe_2$, $-NPr^n_2$, $-NPr^i_2$, $-NBu^{sec}_2$, ethylaniline and 2,6-dimethylpiperidine.

Table 15

$Co\left[OC(CH_3)_3\right]_2$ Nujol mull (cm^{-1})		$Co\left[OC(C_2H_5)_3\right]_2$ Nujol mull (cm^{-1})	
1250	s	1260	m
1190	s	1148	s
1029	w	1127	s
932	vs	1035	s
895	w	1017	s
842	w	947	vs
770	m	922	s
725	w	800	s
609	s	780	m
488	m	760	m
397	m	723	w
358	w	695	w
286	m	615	m
264	s	585	s
		525	s
		512	m
		435	m

Fig.22



The visible and near I.R. spectra of $Co\left[OC(C_2H_5)_3\right]_2$ and $Co\left[OC(CH_3)_3\right]_2$

Table 16

Visible and near I.R. spectra (Nujol mulls)

$Co[OC(CH_3)_3]_2$	$Co[OC(C_2H_5)_3]_2$
λ_{max} (cm^{-1})	λ_{max} (cm^{-1})
8,330	8,330
15,750	15,920
17,700	17,540
20,620	19,600
	23,530

The reaction described below is typical in its method and results.

Anhydrous cobaltous bromide (13g.; 0.1 mole) was slowly added to lithium di-n-propylamide (21.4g.; 0.2 mole) dissolved in 150 ml of tetrahydrofuran. During addition the solution was kept at 0°C. The solution initially turned blue then green and finally very dark brown. After stirring for several hours the tetrahydrofuran was removed and pentane added. The solution was filtered and the residue washed with pentane. The residue was shown to be mainly lithium chloride with some unreacted cobalt chloride. The pentane was removed from the filtrate under reduced pressure. A black viscous gum was obtained. This was slowly heated under vacuum 10^{-4} mm Hg using a liquid nitrogen cold finger condenser directly above the reaction flask. Between 50°C and 60°C (bath temperature) a white solid was collected on this cold finger. Above 80°C this solid became quite voluminous and was removed from the cold finger into a cold trap. The flask was heated to 140°C but no other compound was sublimed onto the cold finger. The residue in the flask was a black solid which contained a high percentage of cobalt.

Co (found) 35.5% required for Co $\left[N(CH_2CH_2CH_3)_2\right]_2$ 22.8%.

The white solid collected in the cold trap was later shown by V.P.C. to be di-n-propylamine.

All other experiments where heating under vacuum was employed gave similar results so it was decided to try an amine with a large steric effect under conditions where no heat was employed.

Anhydrous cobaltous bromide (2.69.; 12.3 m.mole) dissolved in tetrahydrofuran (25 ml) was added very slowly to lithium 2,6-dimethyl-

piperidide and the solution stirred and kept at 0°C. The initial blue solution changed to green. After addition, the solution was stirred for several hours at 0°C. The solution was filtered and the solvent of the filtrate removed under vacuum. A green solid resulted which became black and sticky in the presence of oxygen. This could not be purified by normal means as it decomposed on heating and was very soluble in non-polar solvents and could not be recrystallised. The solid was re-extracted with pentane and analysed.

Co (found) 21.3% N (found) 9.68% Li 0.1% Br 0.1%

The nitrogen analyses was performed by the Kjeldahl method as distillation from a strongly alkaline solution gave low results even for the free amine. The analyses required for cobalt bis-2,6-dimethyl-piperidide are given below:-

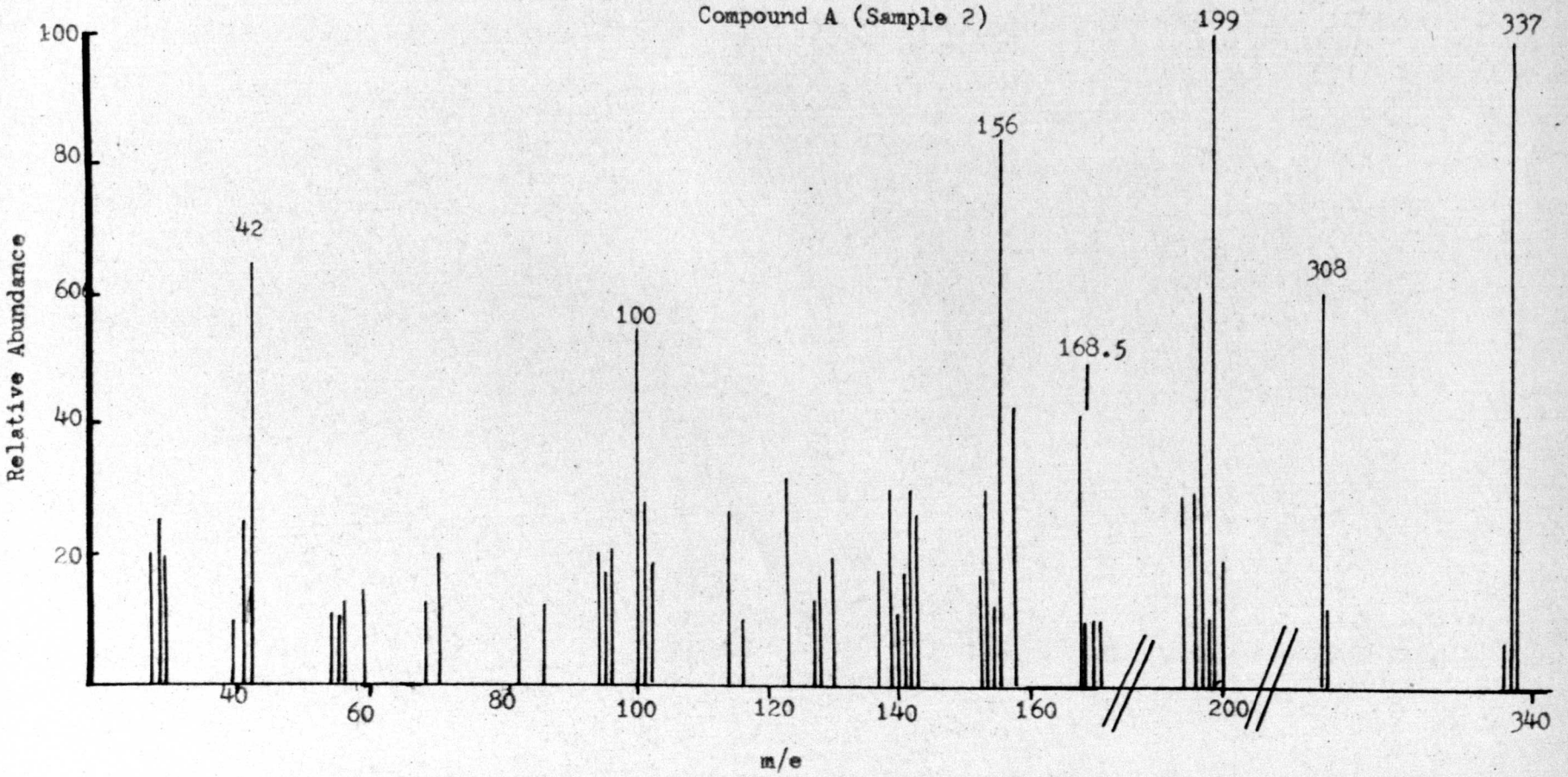
Co 20.8% N 9.90%

The I.R. spectrum could not be obtained due to the sensitivity to oxygen of the compound. The U.V. and visible spectra were tried several times in solution and as nujol mulls between glass plates, but again, the oxygen sensitivity of the compound made this very difficult. A possible band was observed in a nujol mull at $\sim$15,550 cm^{-1}.

When this compound was reacted in solution with tetriary butanol and triethylcarbinol it gave the products isolated from the reaction of these alcohols with hexamethyldisilylamino cobalt (II).

Fig 23

Compound A (Sample 2)



PART I

DISCUSSION OF RESULTS

The Structure of compound A

The stereochemistry of the cobalt atom.

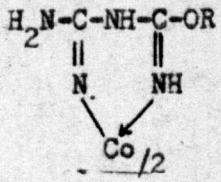
As the compound was monomeric in solution and the U.V. and visible spectra were similar in the pure compound and solution there seemed to be three possible stereochemistries for the cobalt atom.

(a) A square planar arrangement of the four nitrogens around the cobalt.

(b) A tetrahedral arrangement of the four nitrogens around the cobalt.

(c) a higher coordination, (five or six) the extra coordination caused by hydride formation, the formation of an alkylcobalt compound similar to the alkylcobalamins or association in the pure compound.

(a) Planar complexes of cobalt (II) are almost invariably low spin complexes and so have magnetic properties indicative of one unpaired electron. Thus cobalt phthalocyanine has a magnetic moment at 300°K of 2.72 B.M. and at 90°K of 2.22 B.M.[54]. Other square planar complexes of cobalt (II) (where nitrogen ligands are involved) are quite plentiful and a fairly good example of these are the complexes of O-alkyl-1-amidinourea[55].



These have been shown to be isomorphous with the nickel (II) complexes which are square planar. The complexes (where R = Et, Pr^n, Pr^i, n-Bu) have been shown to have a magnetic moment of 2.3 B.M. which is slightly temperature dependent becoming 2.2 B.M.at 105°K. Their spectra are very

similar to compound A having two main bands at 10,000 cm^{-1} and 23,500 cm^{-1}.

The only reported high spin square planar complex of cobalt (II) was the acetylacetonate reported by Cotton and Holm[56]. This result was later rejected by Cotton and Soderbury[57] because of the evidence of association in solution leading to octahedral coordination of the cobalt (II.) The crystal structure later showed this to be correct and the compound consisted of octahedral tetrameric units in the crystal.

Certain α,β unsaturated β - ketoamine complexes of cobalt (II) have been shown to have a planar-tetrahedral equilibrium in solution[2]. (this will be discussed in the next section). The truly planar α,β unsaturated β-ketoamine complexes again have magnetic moments for one unpaired electron (2.3 B.M.). Thus it appears that a planar configuration for this complex can be ruled out by the magnetic moment (4.14 B.M.) and its apparent temperature independence (within experimental error). A planar complex of cobalt (II) surrounded by four nitrogens would almost certainly have a value for the magnetic moment consistent with one unpaired electron.

(b) Tetrahedral complexes of cobalt (II) generally have magnetic moments which lie in the range 4.4 to 4.7 B.M. The d^7 ion in a tetrahedral field has an $^4A_2$ ground state and so the orbital angular momentum is quenched. The departure from the spin-only value for a d^7 ion (3.88 B.M.). is the result of spin-orbit coupling which decreases with increasing ligand field strength. Thus ligands which give low moments are exhibiting a strong ligand field and those giving high moments are exhibiting a weak ligand field. The moments of tetrahedral cobalt (II) compounds are generally independent of temperature.

The spectral properties of a d^7 ion in a tetrahedral environment have been shown to consist of three transitions in the visible and near I.R. regions of the spectrum. The approximate values and assignments are:-

ν_1	ν_2	ν_3
3000 - 5000 cm^{-1}	4000 - 8000 cm^{-1}	15,000 - 20,000 cm^{-1}
$^4A_2 \longrightarrow {}^4T_2$ (F)	$^4A_2 \longrightarrow {}^4T_1$ (F)	$^4A_2 \longrightarrow {}^4T_1$ (P)

ν_1 is a weak band and because it occurs in the near I.R. region has been little observed. ν_2 and ν_3 are more intense and broad, often exhibiting fine structure caused by spin-orbit coupling. Ballhausen[44] using the Bethe-Van Vleck crystal field model and the approximation of single electron excitation showed that:-

$$\frac{f(\nu_3)}{f(\nu_2)} \approx 10$$

Generally the values of this ratio are less than ten, as shown from the values obtained from Table 1.

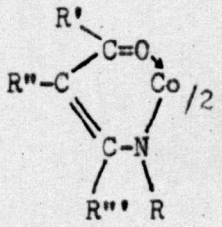
$(CoCl_4)^{2-} = 7.1$	$(CoBr_4)^{2-} = 8.3$
$(CoI_4)^{2-} = 7.3$	$Co(CNS)_4^{2-} = 4.1$

The ratio obtained for compound A in ethanol solution was 12.0. This value was much greater than generally obtained for tetrahedral cobalt (II) compounds, but this effect may be due to 'intensity stealing' from the high energy charge transfer band at 29,850 cm^{-1}.

Cotton and Holm[43] first pointed out that the effective magnetic moment is inversely proportional to the ligand field strength and the spectrochemical series of some of the ligands they used increased

in the series I^- Br^- SCN^- $-NCO^-$ $-NCS^-$. Thus nitrogen ligands create the largest ligand fields (in the series shown) and so the lowest magnetic moments. Compound A has a magnetic moment of 4.14 B.M., which is lower than generally observed and also the bands which may be assigned to ν_3 and ν_2 (22,150 and 10,000cm^{-1} respectively for the pure compound) are of higher energy than generally observed.

Some α,β unsaturated β- ketoamine complexes of cobalt have also shown the same tendency[2].



For example, the compound where R = i-C_3H_7; R' = CH_3; R" = H; R"' = CH_3 has an effective magnetic moment of 4.35 B.M. in the solid and the spectrum as a nujol mull gives ε_{max} of 19,000 cm^{-1} and 8,400 cm^{-1}. Solution spectra of the above and similar complexes show these bands to have rather low extinction coefficients which may be due to distortion from strict tetrahedral symmetry. Other α,β unsaturated β - ketoamines have been shown to exist in a planar-tetrahedral equilibrium in solution. Substituting R = H in the above complex gives a compound with a magnetic moment in the solid state of 2.23 B.M. and in chloroform solution of 3.86 B.M. There are also distinct changes in the spectra of the solid and the solution.

(c) The lack of I.R. evidence (no band assignable to a possible Co-H stretching mode) tends to rule out the possiblity of a hydride complex. The presence of an alkyl cobalt complex seems improbable because of the reformation of compound A from the ligand hydrochloride

and a cobalt halide in the presence of a strong base. Alkyl cobalt compounds have generally been prepared by the reaction of alkyl halides with a cobalt (I) hydride complex of a tetradentate nitrogen ligand[58] or by the reaction of a cobalt (III) complex with a Grignard reagent[59]. Association is ruled out because the molecular weight in solution (over a reasonable concentration range) appears to be that of the monomer. Also the visible and near I.R. spectra in solution are very similar to those of the pure compound.

Compound A has been shown to fit best a tetrahedral arrangement of four nitrogens around the cobalt. It must be stressed that tetrahedral in this context really means 'pseudo' tetrahedral as even in simple systems such as $(CoCl_4)^{2-}$ X-ray diffraction has shown that all the Co-Cl bond lengths are not the same and the angles all differ from a normal tetrahedral angle.

Using the spectral and magnetic data in a tetrahedral model enables values of certain parameters to be calculated. The significance of these values will now be discussed.

<u>The ligand field strength (Dq) and interelectronic repulsion (B)</u>

Tanabe and Sugano[60] have calculated the energy differences between the ground term and the other main terms for d^n systems. These energy differences are calculated from a crystal field model using Racah interelectronic repulsion parameters B and C. For a d^7 ion in a tetrahedral configuration the energy differences are shown below:-

$$^4A_2 \rightarrow {}^4T_2\ (F) = \nu_1 = 10\ Dq \qquad (1)$$

$$^4A_2 \rightarrow {}^4T_1\ (F) = \nu_2 = 15\ Dq + \frac{15}{2}\ B - Q \qquad (2)$$

$$^4A_2 \rightarrow {}^4T_1(P) = \nu_3 = 15\,Dq + \frac{15}{2}B + Q \quad (3)$$

$$\text{Where } Q = \tfrac{1}{2}\left[(-6Dq + 15B)^2 + 64(Dq)^2\right]^{\frac{1}{2}} \quad (4)$$

Using the values given in Table 4 and assuming that the lowest energy transition was ν_1 we obtain the following values from equations (1), (2) and (3).

$$Dq = 590\ cm^{-1} \qquad B' = 944\ cm^{-1}$$

The ratio of the Racah parameters C/B for the first transition series is generally around 4 and in the case of a d^3 ion in an octahedral field or a d^7 ion in a tetrahedral field it has been assumed to be 4.50 and therefore $C' = 4{,}248\ cm^{-1}$.

Using equation (4) to check the validity of these results a value of $5{,}800\ cm^{-1}$ is calculated as compared with the observed value of $6{,}125\ cm^{-1}$. The accuracy seems quite fair as the positions of ν_1, ν_2 and ν_3 have been taken from the positions of maximum absorption. Taking values of $10Dq = 6{,}000\ cm^{-1}$ and $5{,}800\ cm^{-1}$ gave values of Q of $5{,}760\ cm^{-1}$ and $5{,}590\ cm^{-1}$ respectively. B was first calculated giving values of $924\ cm^{-1}$ and $962\ cm^{-1}$ respectively.

The value of 10 Dq is very high, generally values for tetrahedral compounds are $< 5000\ cm^{-1}$ examples are shown in Table 1. Thus the ligand comes very high in the spectrochemical series for tetrahedral cobalt (II).

The free ion value of B for Co (II) is $972\ cm^{-1}$. B is reduced when the metal ion is complexed and ligands may be arranged in the order in which the value of B increases towards the free ion value. This arrangement of the ligands (and metal ions) is called the nephelauxetic series and the ligand from compound A is very high in this series. The value of B' generally seems to increase with increasing

ligand field strength although the nephelauxetic series is not identical to the spectrochemical series. Generally nitrogen ligands are high in both series.

The temperature independent paramagnetic effect (T.I.P.)

Tetrahedral Co (II) has an $^4A_2$ ground term and with this ground state all the energy levels are $\gg kT$ - above the ground levels. There is no first order Zeeman effect with this ground state but there is a second order Zeeman effect which is independent of temperature. This effect is small compared with the overall susceptibility of the compound but is too large to be neglected. The susceptibility due to the second order Zeeman effect has been shown to be equal to $\frac{8N\beta^2}{10\ Dq}$ for an A_2 term. β is the Bohr Magneton and N is Avogadro's number. This gives a value of 350 c.g.s. for compound A. This value has been used in the experimental section for the calculation of the effective magnetic moment.

Spin-orbit coupling constant.

As stated before the departure from the spin-only value of the magnetic moment is caused by spin-orbit coupling. The free ion value for the spin-orbit coupling constant (λ_o) is 178 cm^{-1} and this falls considerably when the metal ion is complexed. The reduced constant (λ^1) is related to the free ion value by the factor k^2 i.e.

$$\lambda^1 = k^2\lambda_o$$

k is an electron delocalization factor which is dependent upon the mixing of the ligand orbitals with the metal orbitals. When there is no delocalization k = 1. Thus k and λ^1 are interrelated and may be calculated in two ways. The magnetic susceptibility observed is related to the spin-only value by the equation

$$\chi_m = \chi_m \text{ S.O.} \left[1 - \frac{8k^2\lambda_o}{10Dq}\right] + \frac{8k^2N\beta^2}{10Dq} \qquad (5)$$

From this equation k may be calculated.

The effective magnetic moment is related to the spin-only magnetic moment by the equation,

$$\mu_{eff} = \mu_{eff} \text{ S.O.} \left[1 - \frac{4k^2\lambda_o}{10Dq}\right] \qquad (6)$$

$$\text{or} \quad \mu_{eff} = \mu_{eff} \text{ S.O.} \left[1 - \frac{4\lambda^1}{10Dq}\right] \qquad (7)$$

from this equation λ^1 may be calculated.

Equation (5) was used to calculate k and from this λ^1 was calculated. This gave the values

$$k = 0.75 \qquad \lambda^1 = -96 \text{ cm}^{-1}.$$

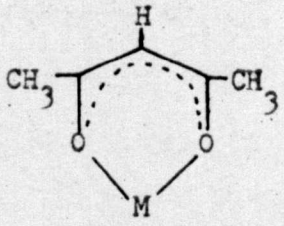
The value of k and thus λ^1 depends critically upon the accuracy of the difference between the measure susceptibility (7,520 c.g.s.) and the susceptibility calculated for the spin-only moment (6,250 c.g.s.). Nevertheless this value of k indicates that there is some delocalization of the metal d electrons onto the ligand.

The I.R. and U.V. spectra of Compound A

The I.R. spectra of compound A the nickel and zinc analogues show very close similarities to the metal acetylacetonates. Thus the metal acetylacetonates show a weak absorption at greater than 3,000 cm^{-1} generally about 3060 cm^{-1}. This has been assigned to a C-H stretching frequency. The position of this C-H frequency is very similar to aromatic C-H stretching vibrations and this is used as evidence of the 'pseudo' aromatic character of the metal acetylacetonates. Compound A shows a weak absorption at 3062 which disappears on deuteration. The

hydrogen on the acetylacetonate ring in the metal complexes is known to be labile and easily replaced by halogens or nitrated[51].

Nakamoto[61] has carried out a normal coordinate analysis on Cu $(acac)_2$ using a 1:1 complex model. The vibration frequencies for other metals have been calculated from the assignments for copper[62].



For cobalt (II) only one frequency was assigned to the stretching of partial double bonded carbon to carbon and carbon to oxygen $\left[\nu(C\text{-}C)\ \nu_8 \text{ and } \nu(C\text{-}O)\nu_1\right]$ this was at 1601 cm^{-1}. The assigned values for nickel (II) and zinc (II) were 1598 cm^{-1} and 1592 cm^{-1}. Whereas for copper (II) and beryllium (II) a different frequency was assigned to each stretching mode. α, β Unsaturated β-ketoamine complexes of metals also showed strong absorptions at about 1570 - 1565 cm^{-1},[51]. Compound A gave a strong absorption at 1565 cm^{-1}. A combination mode of ν(C-O) and a ν(C-H) (ν_9) was assigned at 1513 cm^{-1} and 1461 cm^{-1} for the cobalt (II) acetylacetonate. Compound A also gave strong bands in this region at 1508 cm^{-1}, 1490 cm^{-1}, 1478 and 1440 cm^{-1}. The out-of-plane deformation of the carbon hydrogen on the ring was assigned to 767 cm^{-1} in cobalt (II) acetylacetonate. In compound A a band at 725 cm^{-1} was observed which became greatly reduced upon deuteration suggesting that this hydrogen was attached to a similar ring to that in the acetylacetonates. The U.V. spectrum of compound A showed a high intensity band at 28,800 cm^{-1} with a shoulder at 34,500 in hydrocarbon solution whereas the free ligand gave a band

at 32,300 cm^{-1}. The extinction coefficients were much reduced from that of the free ligand. Similar effects have also been observed for metal acetylacetonates[63], metal α,β unsaturated β- ketoamine complexes[64] and some metal complexes of tetradentatediimine derivatives[52].

Thus 2,4 pentanedione gave an absorption band at 37,200 cm^{-1} with an extinction coefficient of ~12,000. This was assigned to a $\pi \rightarrow \pi^*$ transition. The cobalt (III) complex gave three bands in this region at 38,800 cm^{-1}, 33,900 cm^{-1} (shoulder) and 30,700 cm^{-1} which were assigned to $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and $d_{\varepsilon} \rightarrow \pi^*$ respectively.

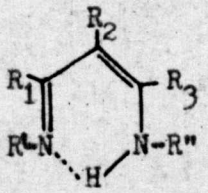
α,β unsaturated β-Ketoamines generally gave absorption bands at ~31,000 cm^{-1} with extinction coefficients of about 17,000 to 20,000. The chromium (III) complexes gave two bands in this region at about 37,600 cm^{-1} and 28,000 cm^{-1} with extinction coefficients of approximately 20,000 and 12,000 respectively.

Some nickel (II) complexes with tetradentatediimine pyrole derivatives also showed the same effect. Thus the free ligands showed absorptions at approximately 35,000 cm^{-1} with extinction coefficients of about 34,000. The nickel (II) complexes gave two bands in this region at approximately 37,000 cm^{-1} and 31,500 cm^{-1} with extinction coefficients of approximately 6,500 and 26,000 respectively.

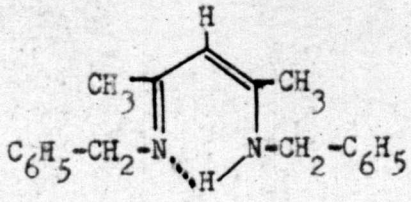
The spectrum of compound A in ethanol was observed to change on standing to give a spectrum similar to the ligand. Ethanol has been shown to be a weak acid pK_A 19.5. It is also very hygroscopic when dry. The change in the spectrum to give a spectrum similar to the free ligand may be due to the action of the water or ethanol as

acids. The visible spectra in ethanol were not significantly different to the spectra in cyclohexane, but the concentration of the solutions used for the visible spectra was approximately 1×10^{-3}M, whereas that used for the U.V. spectra was approximately 3×10^{-5}M.

The similarity of the I.R. and U.V. spectra of compound A to the acetylacetonates and α,β unsaturated β-ketoamines indicated that the ligand of compound A may be an iminoamine of the form.



This was supported by a mass spectrum of the ligand giving a possible molecular ion at m/e 140 and some evidence from the mass spectrum of compound A (see later) indicating that there were two bidentate and not one tetradentate ligand attached to the cobalt atom. The main fully hydrogenated product of the hydrogenation of compound A being 1:3 bisethylaminobutane also indicated the possibility of the ligand being an iminoamine. There was only one α,β unsaturated iminoamine of this type known, this was 2,-benzylamino-4-benzylimino-2-pentene[65] shown below



This will be discussed in the next section with reference to the ligand and ligand hydrochloride.

The ligand, ligand hydrochloride and zinc complex.

As these three compounds are the diamagnetic derivatives obtained from compound A, they are most usefully discussed together.

The I.R. spectra of the ligand and ligand hydrochloride show very strong bands at 3,250 cm^{-1} and 3,220 cm^{-1} respectively. The ligand hydrochloride also showed a series of weak to medium bands between 2,700 cm^{-1} and 2,050 cm^{-1}. Upon deuteration of the ligand hydrochloride the band at 3,220 cm^{-1} was very greatly reduced and a new strong band at 2,320 cm^{-1} appeared.

Primary amines generally show two bands in the range 3,500 cm^{-1} to 3,300 cm^{-1} and secondary amines show one band in this region. In both primary and secondary amines this N-H stretching vibration frequency is lowered by inter- and intra molecular bonding. The hydrochlorides of secondary amines have been examined by Heacock[66] who found a complex series of absorptions between 2,800 cm^{-1} and 2,000 cm^{-1}. These bands upon deuteration were considerably reduced and a number of intense bands appeared between 2,400 cm^{-1} and 1,900 cm^{-1}. These were almost certainly associated with the $-\overset{+}{N}D_2$ stretching mode.

2-Benzylamino - 4-benzylimino — 2 — pentene gave a band (which was weak and broad) between 3,340 cm^{-1} and 2,500 cm^{-1} which on deuteration disappeared and a new band was found at 2,270 cm^{-1}.

Both the ligand and ligand hydrochloride showed two very strong absorptions at 1640 cm^{-1} and 1590 cm^{-1} altered only very slightly on deuteration of the ligand hydrochloride.

Unconjugated imines generally shows strong I.R. absorptions between about 1680 cm^{-1} to 1660 cm^{-1} depending very much on the

environments of the -C=N- grouping. Conjugated imines show a shift to lower frequency and also conjugation with a C=C group generally leads to multiple frequencies between about 1640 cm^{-1} and 1570 cm^{-1}.

2-Benzylamino-4-benzylimino-2-pentene gave two bands in this region at 1620 cm^{-1} and 1560 cm^{-1} which were assigned to the conjugated C=C and C=N groups. The small shifts on deuteration of the ligand hydrochloride are probably caused by the removal of the coupling of these vibrations with the N-H deformation frequency which probably occurred at about 1600 cm^{-1}. Heacock had found with the amine hydrochloride absorptions in the region between 1620 cm^{-1} and 1560 cm^{-1} which upon deuteration disappeared and two new bands at approximately 1290 cm^{-1} and 1240 cm^{-1} appeared. Heacock proposed that one or both of these bands was associated with the deformation of the $-\overset{+}{N}D_2$ group. The ligand hydrochloride showed some definite changes in this region but no bands directly assignable to a $-\overset{+}{N}D_2$ deformation. One new strong band appeared upon deuteration at 1117 cm^{-1} and there were other changes in the spectrum between 1300 cm^{-1} and 1100 cm^{-1} as shown in Tables 8 and 9. The band at 1117 cm^{-1} may be the $-\overset{+}{N}D_2$ deformation although this value seems to be low.

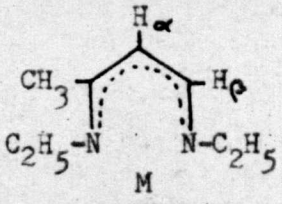
All aromatic amine hydrochlorides also absorbed near 800 cm^{-1} and this was tentatively assigned to the $-\overset{+}{N}H_2$ rocking mode but there would probably be some coupling with the out-of-plane C-H deformation on the aromatic ring, which occurred in this region. The ligand hydrochloride possessed a medium and two strong bands at 835 cm^{-1}, 788 cm^{-1} and 745 cm^{-1} which, on deuteration, disappeared and the bands which appeared at 595 cm^{-1} and 555 cm^{-1} may have been their deuterated equivalents.

The U.V. spectra of the ligand and ligand hydrochloride were similar to each other as were the U.V. spectra of 2-benzylamino-4-benzylimino-2-pentene and its hydrochloride. The latter compounds, gave a single absorption maximum at 31,100 cm^{-1} and 31,200 cm^{-1} with extinction coefficients of 39,800 and 41,600 respectively. This was added evidence for the similarities of the ligand to 2-benzylamino-4-benzylimino-2-pentene.

C-N stretching frequencies in aliphatic amines generally occurred in the region 1220 cm^{-1} to 1020 cm^{-1}. The ligand and ligand hydrochloride showed several strong or very strong bands in this region. Obviously no particular frequency may be assigned to this vibration especially as it will be coupled with the conjugated imine system. If the system is 'pseudo' aromatic as in the acetylacetonates the C-N bonds will be equivalent and have a large degree of double bond character. From the foregoing results and comparisons it appeared that the ligand was probably a conjugated imine system and also that it probably possessed a secondary amine system. The similarity to 2-benzylamino-4-benzylimino-2-pentene was striking.

The zinc compound prepared from the ligand did not show the N-H frequency at ~3,200 cm^{-1}. There was a lowering of the frequencies in the 1500 cm^{-1} region (discussed before). The U.V. spectrum also showed a shift of the charge transfer band to lower frequency from the ligand.

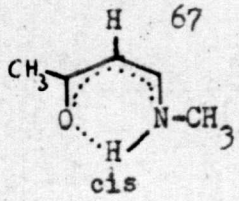
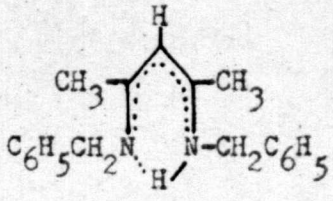
The N.M.R. spectra of the zinc compound, the ligand and the ligand hydrochloride used in conjunction with all the other evidence discussed before indicated the following structure:-



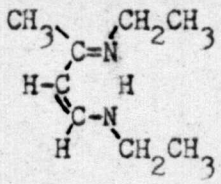
where M = Zn/2 or H

The chemical shifts, the coupling and ratios of the protons may all be accounted for in the above structure. The table below shows the assignments of the protons and comparison with an analogous α, β unsaturated β -ketoamine and 2-benzylamino-4-benzylimino-2-pentene. All spectra used deuterchloroform as solvent and the chemical shifts were measured using T.M.S. as internal standard.

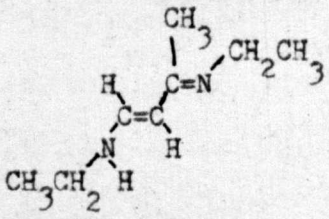
Table 16

	CH_3-(N-Et)	CH_2-N	CH_3-C	H_α	H_β	N-H
	ppm	ppm	ppm	ppm	ppm	ppm
Zinc compound	1.05	3.19	1.89	4.05	7.00	-
ligand	1.23	3.35	2.29	5.40	7.69 7.96	9.12
ligand hydrochloride	1.17	3.38	2.42	5.10	7.82	9.95, 9.69
 67 cis	-	2.98	2.02	4.98	6.62	9.6
	-	4.44	1.92	4.63	-	11.5

The ligand might exist as a cis or a trans isomer or both.



cis



trans

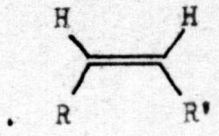
The α,β unsaturated β-ketoamine in table 17 was shown to exist as the cis and trans isomers in equilibrium. The N.M.R. spectrum of this compound showed that the neat liquid consisted almost entirely of the trans isomer. A1.0.M solution in chloroform on the other hand showed that predominant species was the cis isomer. 2-Benzylamino-4-benzylimino-2-pentene in contrast was shown to exist entirely as the cis isomer in deuterochloroform solution.

Banwell[68] had shown that cis and trans hydrogens on a substituted ethylene had very different couplings in their N.M.R. spectra. These couplings were related by the following equations.

$$J \text{ cis} = 11.7\ (1 - 0.34\,\Delta E)$$

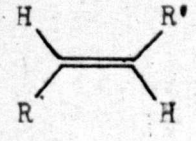
$$J \text{ trans} = 19.0\ (1 - 0.17\,\Delta E)$$

Where J_{cis} and J_{trans} were the couplings of the hydrogens on the substituted ethylene.



cis

or



trans

The values 11.7 c/s and 19.0 c/s were the observed values for the parent hydrocarbon ethylene. ΔE was the difference in electronegativity between R' and R" and the hydrogens that they replace. Thus values of J_{cis} for substituted ethylenes were found to be in the range (3 - 10 c/s) whereas the J_{trans} values were higher in the range (9 - 20 c/s).

The α,β unsaturated β-ketoamine shown in Table 17 gave a cis hydrogen coupling of 7.4 c/s and trans coupling of 13.3 c/s. The ligand and ligand hydrochloride did not give sharp signals for the H_α and H_β protons but in the zinc compound a coupling of 8.0 c/s was found for these protons. This indicated a cis structure for the zinc compound. The ligand and ligand hydrochloride on the other hand showed very broad regions of absorption for the H_α and H_β protons and this could indicate that a mixture of cis and trans isomers were present.

The ethyl groups attached to the nitrogens showed a coupling of 7.4 c/s in the ligand and ligand hydrochloride. This was consistent with the values given by Banwell in the equation:-

$$J\ (CH_3CH_2X) = 7.9\ (1 - 0.09\Delta E)$$

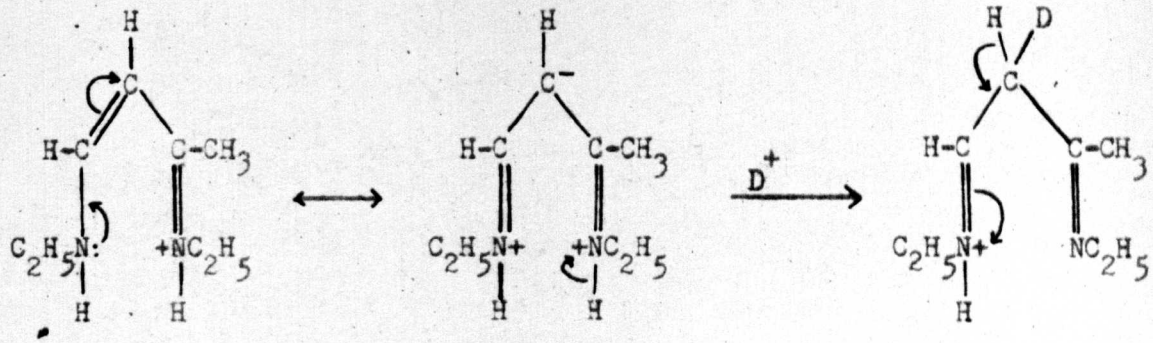
ΔE was the difference in electronegativity between X and the hydrogen in ethane.

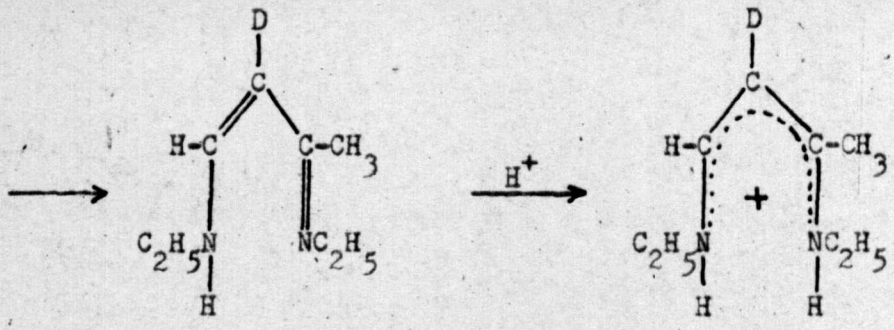
The ligand gave two equal overlapping triplets for the methyl group (in the C_2H_5N- group). The CH_2-N region also consisted of possibly two overlapping quartets which could have indicated the presence of cis and trans isomers.

The zinc compound gave two overlapping quartets for the $-CH_2-N$ protons. The nonequivalence of the $-CH_2-N$ protons may be due to the unsymmetrical character of the ring caused by the methyl group attached to the ring. This was supported to some extent by the fact that on deuteration of the zinc compound the $-CH_2-$ protons were effected and caused a slight change in the spectrum. Another possibility was that the zinc compound with an almost tetrahedral

zinc atom was an asymmetric molecule. Methylene protons have been shown to be rendered slightly nonequivalent if they were close to an asymmetric centre[69]. Another possibility was that the ethyl groups on the nitrogen were restricted in rotation by steric effects. "Dreiding stereomodels" showed that this latter explanation was probably a valid one, although large distortion of a tetrahedral zinc atom might cause the ethyl groups to have sufficient volume in which to rotate.

. Deuteration of compound A and the zinc analogue was shown to take place quite rapidly. The N.M.R. spectrum of the deuterated zinc compound showed that the H_{α} proton was exchanged. The N.M.R. spectra of the ligand and ligand hydrochloride in deuterium oxide showed the absence of this proton and thus it had been exchanged. Even in deuterochloroform this proton did not give a sharp signal. A possible explanation of this observation may be that the ligand and ligand hydrochloride could not be thoroughly dried and water present may have been exchanging with this proton. A possible mechanism of exchange of this proton is shown below.





The slight excess of protons in the 1 ppm region in the spectra of the zinc compound was probably due to some unremoved hydrocarbon initially used to dissolve the compound after sublimation.

As shown in Fig.10, compound A gave an N.M.R. spectrum. Cobalt (II) compounds are increasingly being shown to give proton magnetic spectra. Early work in this field by Milner and Pratt[70] with diamine complexes of cobalt (II) showed that each type of proton gave one signal which was often broad and showed large chemical shifts from the spectra of the diamagnetic diamines. For a paramagnetic compound to give an N.M.R. spectrum, an electronic relaxation time of 10^{-6} - 10^{-8} sec^{-1} was required. Nuclear relaxation times are related to electronic relaxation times; generally a short electronic relaxation time gives rise to a long nuclear relaxation time, which in turn gives rise to sharp signals. The nuclear relaxation times for cobalt (II) compounds are shorter than normal and give rise to broad signals.

The sharpest signal observed in the spectrum of compound A was the signal at + 36 ppm. which was approximately 180 c/s wide at half height. The two signals at -182 ppm and - 163 ppm. stretched over 3,000 c/s (50 ppm. at 60 Mc/s). The ratios of intensities of the signals were 2:2:12:8:6:<1 for the signals at -182, -163, +36, (+56 and +71), +90 and +117 ppm. respectively. The assignment of these signals can only

be tentative considering the intensities observed. The largest signal at +36 ppm. which was shifted the least from the normal diagmagnetic positions was probably the CH_3- protons of the ethyl groups on the nitrogens. The two signals at +56 and +71 ppm could not be separated and because of their similar intensity these two signals were assumed to be due to the CH_2 groups of the ethyl on the nitrogen. These groups would be slightly inequivalent because of the CH_3 group attached to the ring. The signal at +90 ppm was assumed to be this CH_3 group. The two signals at -182 ppm and -163 ppm. are assumed to be the H_α and H_β protons. The signal at -117 ppm. cannot be assigned under the structure shown. If this signal was assigned to one proton then the total number of protons was much greater than thirty and this was against other evidence such as analysis, mass spectrum and molecular weight determinations. It was noted that the mass spectrum of a freshly distilled sample of compound A gave molecular ion at m/e 337 and an ion at m/e 338 approximately 20% of the intensity of the molecular ion. This was reasonably consistent with a molecule containing 16 carbon atoms and 30 hydrogen atoms. A sample of compound A which had been stored for some time under nitrogen gave an ion at m/e 338 which was 45% of the molecular ion. The position of this band in the N.M.R. spectrum suggested that this was possibly due to a proton attached to a nitrogen due to some decomposition of the cobalt compound. It was noted that in poorly stored samples there was some evidence of a possible N-H group in the I.R. spectrum.

Mass spectra

As stated in the experimental section compound A gave an accurate molecular ion at m/e 337.181858 and the calculated value for $CoN_4C_{16}H_{30}$

was 337.18015 (using C^{12} = 12.00000 as the standard). The ion at M + 1 (m/e 338) was approximately 20% of the molecular ion which was consistent with the isotopic abundances of C^{13}, H^{2} and N^{15}.

$$16 \times 1.1\ (C^{13}) + 30 \times 0.015\ (H^{2}) + 4 \times 0.37\ (N^{15}) = 19.53\%.$$

The nickel compound gave a molecular ion at m/e 336 consistent with the Ni^{58} isotope which had a natural abundance of 67.8%. An ion was also observed at m/e 338 consistent with the Ni^{60} isotope which had a natural abundance of 26.2%. The ratio of the intensities of these ions was 2.67:1 and that required from their natural abundances was 2.59:1. There were also three much smaller ions at m/e 339, m/e 340 and m/e 342 which could be the isotopes Ni^{61}, Ni^{62} and Ni^{64}.

The deuterated compound A showed the following ions in the molecular ion region, m/e 337, m/e 338, m/e 339, m/e 340, m/e 341 and m/e 342. The major ions were at m/e 338, m/e 339 and m/e 340. These would correspond to mono-di- and tri- deuteration. The ion at m/e 341 was only slightly greater than required for the isotopic natural abundance from the ion at m/e 340. It has already been shown that two protons were very easily deuterated (H_{α} protons) and it seemed possible that the H_{β} proton might also be exchanged with deuterium. The approximate composition of the mixture calculated from peak intensities was nondeuterated 19%; monodeuterated 29%; dideuterated 21%; trideuterated 28% and quadrideuterated 3%, (natural abundance 1.2%, 3.7% and 1.1% respectively).

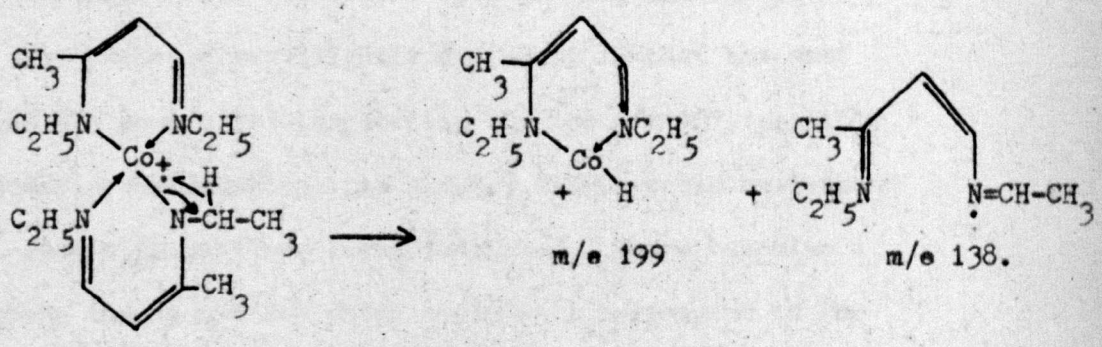
The zinc compound gave a large ion at m/e 337, probably due to the presence of compound A contaminating the zinc compound. Possible molecular ions for the zinc analogue were shown at m/e 342, m/e 344,

m/e 345 and m/e 346 corresponding to the isotopes Zn^{64}, Zn^{66}, Zn^{67} and Zn^{68} respectively.

The discussion of the fragmentation pattern of these compounds can only be qualitative and so possibly open to some conjecture. Two different samples of compound A were recorded at different inlet temperatures. Sample 1 in Fig.4, was run at an inlet temperature of 200°C (10^{-6} mm Hg. pressure) and Sample 2 in Fig.3 was run with an inlet temperature of 285°C (10^{-6} mm Hg pressure). Sample 2 was an older sample than No.1 (as explained previously when discussing the N.M.R. spectrum). Even so, it was noted that Sample 2 gave slightly greater proportions of the lower ions compared to the molecular ion. The nickel compound which was run at the same temperature as Sample 2 showed very little fragmentation except for the main base peak at m/e 198. The zinc compound on the other hand showed considerable fragmentation as did the deuterated compound A. This may be some guide to the thermal stability although the large amount of fragmentation of the deuterated compound A was puzzling.

The most important feature of the spectra of compound A was the ion at m/e 199. This ion was as strong as the molecular ion and in one case the base peak. The deuterated compound A shows this ion at m/e 200 and a slightly weaker ion at m/e 201. The loss of a particle of mass 138 from compound A was a loss of half the organic part except for one proton. Metal acetylacetonates have been shown to lose acetylacetone groups progressively. It seemed possible that the organic part of the molecule was two similar ligands and to obtain the ion at m/e 199, one ligand was lost leaving one hydrogen on the cobalt.

A possible mechanism for this fragmentation is shown below.



Of course it is possible that there are two different ligands which differ by two protons and the smaller was easily removed. This did not seem to satisfy other evidence such as the N.M.R. of the zinc compound and the ligand. The possibility of a tetradentate ligand being present may not be ruled out but all possible formulations for a tetradentate ligand would require the fission of at least one and possibly two carbon-carbon bonds to obtain the required ion. It was thought that the fission of a cobalt-nitrogen bond and the subsequent formation of a conjugated imine system would be more favourable.

With the nickel compound the formation of the ion at m/e 198 (for Ni^{58}) was found to be the major step and there was also much less fragmentation to give lower weight ions.

The deuterated compound A gave the most intense ion in this region at m/e 200 which would correspond to the ion containing one deuterium atom. This is quite consistent with the removal of one ligand and the H_{α} proton on the remaining ligand being substituted with deuterium (the original compound A gave a peak at m/e 200 which was only slightly greater than the natural abundance). There were also fairly intense ions at m/e 199 and m/e 201. The former probably corresponded to the

original compound A and the latter may have corresponded to the dideuterated ligand with the cobalt atom and one hydrogen.

The zinc compound was slightly different in that the most intense ion was at m/e 203 (neglecting the ion m/e 337, possibly from compound A contaminating the sample). This would correspond to a Zn^{64} atom with just one ligand attached. There was also a fairly strong ion at m/e 204 which could well correspond to the Zn^{64} equivalent of the ion at m/e 199 in compound A. The pattern of the rest of the ions to m/e 209 was one of decreasing intensity and because of the possibility of two types of ion for each zinc isotope, the isotopic pattern was masked.

The conjugated diimine radical m/e 138 formed in the fragmentation to give the m/e 199 ion was not observed in the fragmentation patterns of the nickel and zinc analogues. A very small amount of ion at m/e 138 was observed in the spectrum of compound A but a much larger intensity ion at m/e 139 was observed.

Double charged ions were observed in the spectra of compound A at m/e 99.5 and m/e 168.5 corresponding to the ions at m/e 199 and m/e 337 respectively. The nickel compound gave a very small double charged ion at m/e 169.5 corresponding to the ion at m/e 339.

The spectra of compound A contained a metastable peak at m/e 281.5 and so there had been a metastable transition during the flight of the initially formed ion m_1. The relationship $\frac{(m_2)^2}{m_1} = m^*$ (where m^* was the value of the metastable peak and m_2 is the charged ion formed after the transition) was used to show that the molecular ion m/e 337

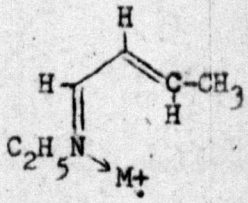
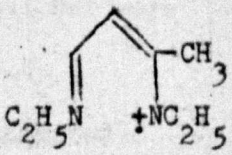
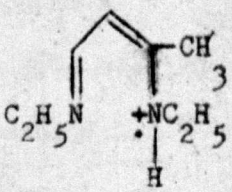
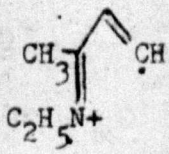
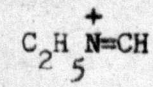
produced an ion at m/e 308 and an uncharged particle of mass 29 units. The ion at m/e 308 was shown in the spectrum. The uncharged particle of mass 29 units might well have been an ethyl group. The deuterated compound A showed the most intense ion in this region at m/e 310 with ions at m/e 309, m/e 311 and m/e 312(lower intensity)although the metastable peak was not observed. The zinc compound showed a main ion at m/e 313 corresponding to the loss of a particle of mass 29 from the main molecular ion at m/e 342.

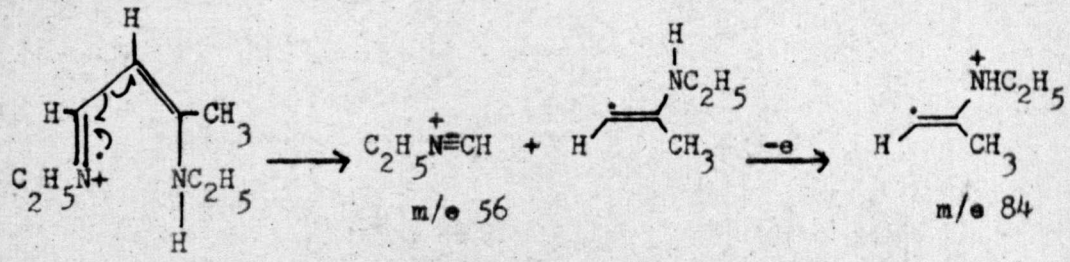
Other important regions of the spectrum which will only be discussed briefly are shown in Table 17.

The fragmentation patterns of these compounds were quite complex and so no definite assignments may be made to the ions. Some ions show quite large abundance in each spectrum and do not change with change of metal atom and so these must be attributed to fragmentation products of the ligand. No spectrum was taken of the ligand but the ligand hydrochloride did give a spectrum shown in Fig.12.

The largest ion of any significant intensity was at m/e 149. This ion could not be explained if the ligand was the proposed aminoimine. The next ions of importance were at m/e 140, m/e 141, which could have been the ligand and its cation respectively. The ion at m/e 125 represented a mass loss of 15 which might well have been a methyl group. The next ion of reasonable intensity at m/e 111 represented a mass loss of 29 which was probably an ethyl group. The base peak of the spectrum was at m/e 84 which may be the ion shown as it may be formed by the initial loss of an ion m/e 56.

Table 17

Compound A	Deuterated Compound A.	Zn^{64}	Ni^{58}	Possible Assignment.
156	156,157,158.	163	155	
139	-	-	139	
140	-	140	140	
96	97	96	96	
56	57	56	56	
42	42, 43	42	42	



The ion at m/e 56 was observed but of low intensity. Ions were observed at m/e 35 and m/e 37, they were not quite in the ratio 3:1 but were probably due to Cl^+ ions.

The mass spectrum of the compound produced after attempted chlorination was almost identical to the spectrum of compound A except that some low intensity ions were observed at m/e 369, m/e 370, m/e 321 and m/e 372. A monochlorinated derivative of compound A would require a molecular ion of m/e 372 for Cl^{35}. Very small ions at m/e 35 and m/e 37 were found which might correspond to Cl^+.

The nickel analogue of compound A.

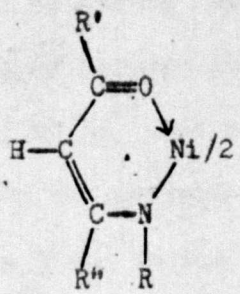
The I.R. spectrum and mass spectrum of the nickel compound prepared from the ligand hydrochloride showed it to be similar to compound A. This compound was shown to be as sensitive to acids as compound A and also probably sensitive to light. Unfortunately a magnetic susceptibility was not obtained which might have helped to deduce the stereochemistry of the nickel atom. An N.M.R. spectrum in cyclohexane did not give sharp lines characteristic of many nickel (II) complexes. The stereochemistry of the nickel atom could only be inferred from the visible spectrum.

The visible spectra of this compound are shown in Fig.14 (a) and (b). The spectrum in cyclohexane was very similar to that in ethanol with minor changes in the frequencies of the maximum absorptions of

the strongest bands in this region. This showed that as with compound A polar solvents did not appear to complex with the metal atom to give higher coordination.

The possible stereochemistries for a tetra coordinated nickel (II) atom were planar or tetrahedral. Nickel (II) forms many diamagnetic planar compounds but this nickel compound was not one of these. Thus the nickel analogue must have been a tetrahedral or 'pseudo'tetrahedral compound of nickel (II). Comparison of the visible spectrum with the visible spectra of other tetrahedral nickel (II) compounds showed this to be the case.

α, β Unsaturated β-ketoamine complexes of nickel (II)[53] have been shown to be planar, tetrahedral or exist in a planar-tetrahedral equilibrium depending mainly upon the group R on the nitrogen.

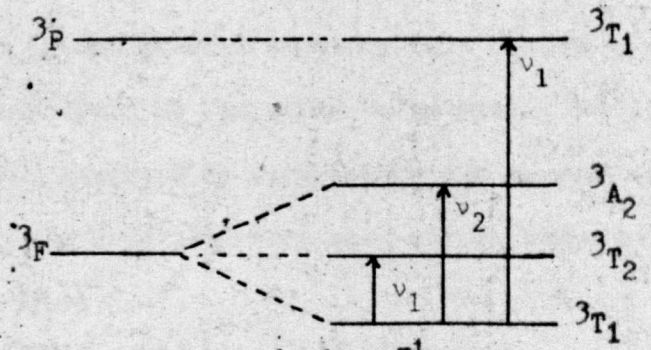


A large group R on the nitrogen producing large steric hindrance e.g. i-C_3H_7 (where R'-R"=Methyl) gave a complex with a magnetic moment of 3.37 B.M. in the solid state and 3.36 B.M. in carbon tetrachloride solution. On the other hand where R=p-$C_6H_4CH_3$ (R'=R"=Methyl) gave a complex which was diamagnetic in the solid state and gave a magnetic moment of 1.23 B.M. in chloroform solution.

The visible spectrum in solution of the tetrahedral complex (where R=i-C_3H_7) showed four main absorptions at 19,200 cm^{-1}, 16,800 cm^{-1}

14,800 cm^{-1} and 6060 cm^{-1} and a very weak absorption at 11,000 cm^{-1}. These values may be compared with the nickel analogue of compound A which gave absorption bands at 22,750 cm^{-1}, 17,150 cm^{-1}, 9,100 and 7,700 cm^{-1} in cyclohexane solution.

A simplified energy level diagram is shown below for tetrahedral nickel (II)..



The absorption band at 6,060 cm^{-1} was assigned to ν_2 in the tetrahedral ketoamine complex. The band at 11,000 cm^{-1} was included with the bands between 14,500 and 19,200 cm^{-1} assigned to ν_3. The band at 11,000 cm^{-1} was possibly a $^3T_1 \longrightarrow {}^1D$ transition as this would have been of the correct intensity expected of such a transition. The assignments given to the visible spectra of bis(N - isopropylsalicylaldimino) nickel (II)[71] (which was found to have a distorted tetrahedral structure) have been contested by Goodgame[72]. This compound gave a band at 6,700 cm^{-1} originally assigned to ν_2 and two bands at 14,100 cm^{-1} and 16,900 cm^{-1} originally assigned to ν_3. These have been reassigned by Goodgame after comparison with the $(NiI_4)^{2-}$ ion[73]. The band at 6,700 cm^{-1} was assigned to ν_1, the band at 14,100 cm^{-1} assigned to ν_2 and the bands at 16,900 cm^{-1} and 19,100 cm^{-1} assigned to ν_3. Thus it maybe that the assignments for the ketoamine complex were incorrect and should have been 6,060 cm^{-1}

(ν_1), 14,800 cm^{-1} (ν_2), 16,800 cm^{-1} and 19,200 (ν_3). Comparisons of compound A with similar ketoamine complex of cobalt (II) showed that the ligand (of compound A) produced a much larger ligand field. The possible assignments for the nickel analogue of compound A taking this into account are 7,700 cm^{-1} and 9,100 cm^{-1} (ν_1) 17,150 cm^{-1} and 22,750 cm^{-1} (ν_3). No band was found which could be assigned to ν_2 but with a strong field in tetrahedral symmetry this becomes a two - electron transition and would be expected to be weak. The intensity of ν_2 in some complexes examined by Goodgame became as weak as that observed for ν_1. Thus ν_2 may have been very weak and so obscured by the tail of the band at 17,150 cm^{-1}.

The nickel (II) analogue of compound A being tetrahedral indicated that a factor such as large steric hindrance of the ligands was taking place. This supported the structure of the ligand shown in the previous section.

The nickel (II) analogue of compound A gave a similar U.V. and visible spectrum to one of the products of the reaction of nickel chloride with lithium diethylamide[47].

Summary of Results.

The preceding sections have shown that compound A was a tetrahedral compound of cobalt (II). As the cobalt atom was surrounded by four nitrogen atoms it was possible that there were four unidentate ligands or two bidentate ligands or one quadridentate ligand or one unidentate plus one tridentate ligand.

The mass spectrum and analysis gave the exact composition of compound A. The I.R. and U.V. spectra of compound A indicated the similarity to acetylacetonates and α, β unsaturated β-ketoamine complexes. The chemical properties, acid sensitivity, ease of deuteration and halogenation also indicated the similarity to the α, β unsaturated β-ketoamine complexes. Collman[51] found that halogenation of α, β unsaturated β-ketoamine complexes of chromium (III) gave much lower yields that halogenation of acetylacetonate complexes and Holm[53] found that some α, β unsaturated β-ketoamine complexes of Ni were air sensitive. The difficulty of reduction of the ligand of compound A indicated the 'pseudo' aromatic character of compound A. The main product of the reduction being 1,3 bisethylaminobutane showed that the ligand was most probably bidentate and that each nitrogen possibly had an ethyl group attached to it. This was supported by the evidence that the nickel compound was tetrahedral and not square planar as in many complexes. Ethyl groups on each of the nitrogen would cause very large steric hindrance and Holm[53] had shown that tetrahedral α, β unsaturated β-ketoamine complexes of nickel (II) could be produced with a large alkyl group on the nitrogen of the β-ketoamine. The ligand and ligand hydrochloride had similar U.V. and I.R. spectra to the known iminoamine (2-benzylamino-4-benzyl-

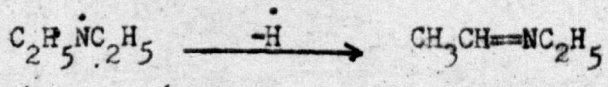
imino-2-pentene). The N.M.R. spectra of the ligand, ligand hydrochloride and zinc complex showed that the ligand was 4-ethylimino-2-ethylamino-2-butene. Thus compound A was bis-(4-ethylimino-2-butene-2-ethylamino) cobalt (II).

One of the main remaining features of this novel synthesis to be explained was the possible mode of formation of compound A from lithium diethylamide and cobalt chloride. This will be attempted in the next section.

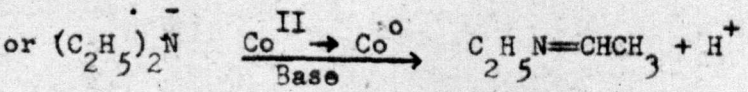
A possible reaction mechanism for the formation of compound A

The following mechanism is proposed for the formation of compound A. The mechanism is divided into four stages and stages I and III have alternate routes and this will be discussed later.

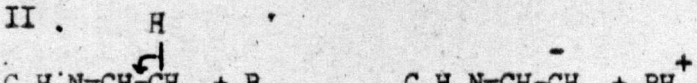
Stage I



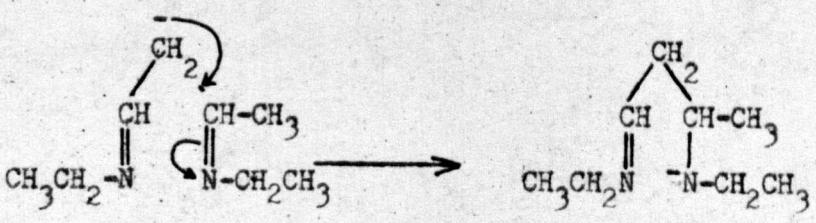
I



Stage II

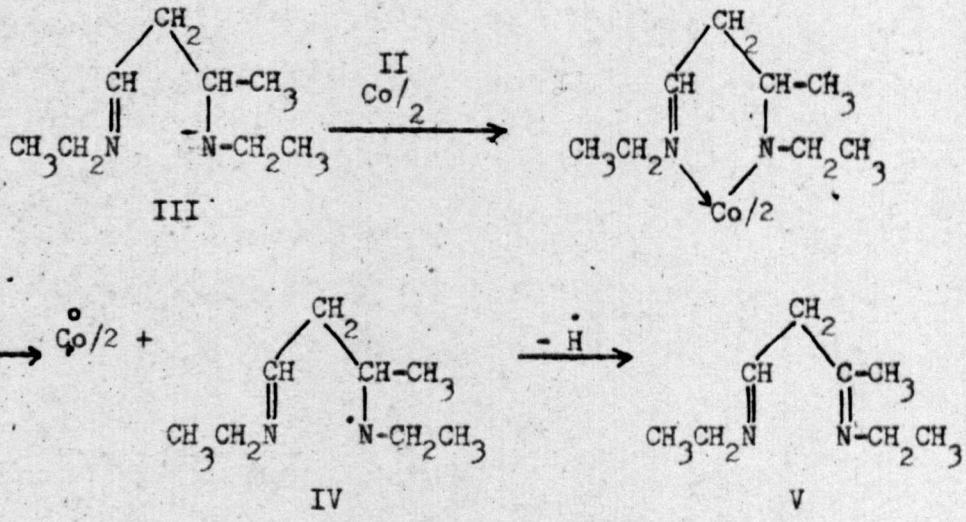


II



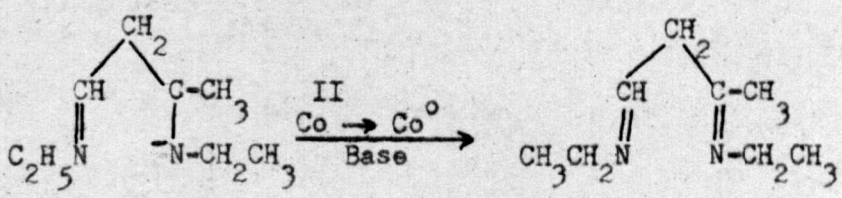
III

Stage III



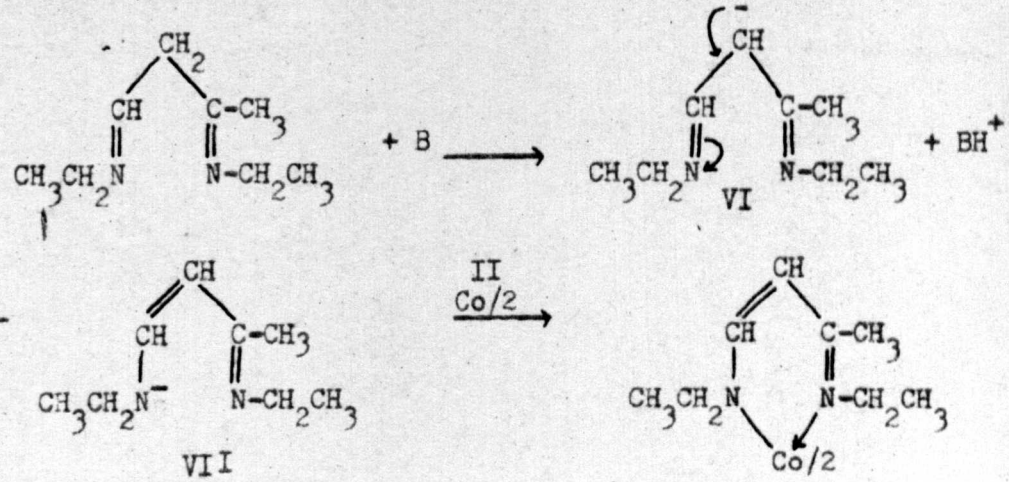
III IV V

OR



III V

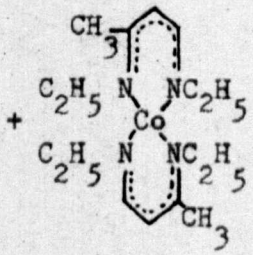
Stage IV



VI VII

The overall reaction is shown in the following equation.

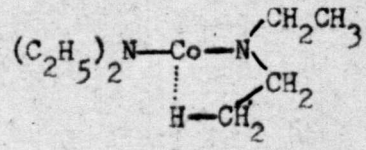
$$7\ CoCl_2 + 14\ LiNEt_2 \longrightarrow 14\ LiCl + 6Co + 10\ Et_2NH$$



The above mechanism seems to fit the facts but much further work would be needed for it to be proved or disproved. The total yield of compound A from the overall reaction equation should be approximately 14.3%. The yields given in Table 2 show that the reaction of 1:2 ratios of cobalt chloride to lithium diethylamide gave yields of about 5-7% whereas ratios of 1:4 of these compounds generally gave yields of 10-14%. The only significant difference excess lithium diethylamide should make if the mechanism is correct is that it will act as a base necessary in the stages of the reaction or that lithium diethylamide plays a large part in Stage I.

Stage I requires the formation of an imine I (ethylidene ethylamine). This may be accomplished by two main methods. The first is the production of an amine radical and loss of a hydrogen radical to give the imine. The most plausible method by which this would be through the initial formation of bis-diethylamino cobalt. The possibility of bis-diethylamino cobalt being formed initially in the reaction seems high. Reactions of cobalt halides with other lithium dialkylamides (where the dialkyl groups are large and will thus cause large steric hindrance) have shown that dialkylamino cobalt (II) compounds exist (see later). These dialkylamino

cobalt (II) compounds appear to be thermally unstable and a diethylamide would be expected to have similar properties. The formation of diethylamino cobalt (II) is supported by the fact that in several reactions almost the quantitative yield of lithium chloride was obtained. The decomposition of bis-diethylamino cobalt (II) could well involve an initial formation of a hydride complex which would itself be unstable because of the high electron density upon the cobalt atom and the difficulty of reducing this by back donation to the ligand.



The products of this decomposition would most probably be diethylamine, cobalt metal and the imine I.

The other possible route for the formation of I might be the oxidation of a diethylamine anion (formed from lithium diethylamide) and the two electron reduction of cobalt (II) to cobalt (0). As shown in Table 2 polar solvents give higher yield of compound A and of course these solvents would enhance the possibility of this route to I. Lithium diethylamide has been shown to reduce benzophenone[74] with the initial formation of I which reacted with excess benzophenone.

Stage II involves the action of a base to form the anion II and then an aldol condensation of this anion II with I. Excess lithium diethylamide would act as a suitable base especially when diethylamine was used as solvent. If the anion III formed were protonated this would be a suitable amine for further aldol condensation with I or itself.

Stage III is the formation of a diimine V from III which may be accomplished in one of two ways. The first route involves the formation of a cobalt compound, its decomposition to form a radical IV with the reduction of the cobalt atom and then loss of a hydrogen radical from IV to give V. This method resembles the first route of stage I. The other possible route resembles the second method of stage I in that a secondary amine anion is oxidized by the reduction of cobalt (II) to cobalt (O) with the formation of an imine (in this case a diimine).

The last stage involves the action of a base upon the diimine V to form an anion Vi which isomerizes to give the conjugated amino-imine anion VII. This then may react to form compound A.

PART II

DISCUSSION OF RESULTS.

Dialkylamino cobalt(II) compounds.

The preparation of these compounds was attempted and the results obtained will be discussed hereinafter.

The bis-hexamethyldisilylamino cobalt (II) showed similar properties to those recorded by Wannagat[37]. Wannagat had predicted that from the volatility of this compound that it was probably a monomer. This was born out by the molecular weight determination carried out in cyclohexane solution which gave a value slightly lower than that required for a monomer. It was probable that this slightly low result was due to a small amount of hydrolysis or oxidation or both. The compound was thus a two co-ordinate cobalt compound which was the only example known of this unusual stereochemistry. The I.R. spectrum of bis-hexamethyldisilylamino cobalt (II) when compared with the I.R. spectra of the zinc, cadmium and mercury analogues indicated a linear N-Co-N grouping. Wannagat[36] had obtained a normal coordinate analysis of the zinc, cadmium and mercury compounds using the metal atom, the nitrogen atoms and the silicon atoms. They found that the metal, nitrogen and silicon atoms were all in one plane and the symmetry of the molecule was D_{2h}. The N.M.R. spectra of these compounds gave one signal showing that all the methyls were equivalent. The compound of cobalt fits well with the assignments for zinc, cadmium and mercury and the comparison is shown in Table 17.

The assignment of the asymmetric nitrogen-cobalt-nitrogen stretching vibration was tentative as only one band was found in the region 400-500 cm^{-1}. As the compound was examined to 400 cm^{-1} it was possible that a band at lower frequency could be assigned to this vibration. Calculated force constants showed that the M-N bond was a covalent single bond for

Table 17.

Hexamethyldisilylamino compounds.

Zn	Cd	Hg	Co	Assignments
1268 s (sh)	1267 s (sh)	1267 s (sh)	1258 vs	$\delta_s(CH_3)$
1257 vs	1255 vs	1257 s	1247 vs	
985 vs	997 vs	979 vs	998-80 vs	$\nu_{as}(NSi_2)$
835 vs	832 vs	836 vs	855-35 vs	$\rho(CH_3)$
674 s	673 s	673 s	672 s	$\nu(SiC_3)$
612 m	616 m	614 m	615 m	$\nu(SiC_3)$
436 s	410 s	406 s	475 m	$\nu_{as}(MN_2)$

vs = very strong; s = strong; m = medium; (sh) shoulder; δ = deformation; ν = stretching; ρ = rocking; s = symmetric; as = asymmetric.

Zn, Cd and Hg. Considering simply mass and coordination number effects of the metal, the frequency of the ν_{as} (N-M-N) vibration for cobalt should be similar to that of zinc (comparison of the tetrachloro complexes shows this effect):-

[75] $(CoCl_4)^{2-}$	[75] $(ZnCl_4)^{2-}$	[76] $(CdCl_4)^{2-}$	[76] $(HgCl_4)^{2-}$
297cm^{-1}	277cm^{-1}	260cm^{-1}	228cm^{-1}

The above tetrahalo-ions showed the same general trend caused by increasing mass as the ν_{as} (MN_2) vibrations in Table 17. The frequency of ν(MX) vibrations generally increases with decreasing coordination number. Cobaltous chloride in the vapour state which was considered to have a coordination number of two exhibited a cobalt-chlorine stretching vibration frequency of 493 cm^{-1} [77]. Zinc chloride in the vapour state exhibited a zinc-chlorine[78] stretching vibration frequency of 516 cm^{-1}, mercuric chloride[79] gave a value of 413 cm^{-1}. Comparing these values with the values for ν_{as} (MN_2) showed that the frequency of 475 cm^{-1} assigned to $\nu(CoN_2)$ was slightly high but of the right order. This high value for the cobalt nitrogen frequency might have been due to increased bond order above a covalent single bond.

The N-Si bonds in the Zn, Cd and Hg compounds showed increased bond order compared to the free amine. The ν_{as} (SiN) frequency in the free amine was 934^{-1} whereas in the metal compounds the frequencies were in the range 980-1000 cm^{-1}. The $\nu_s(NSi_2)$ and $\nu(NSi_2)$ in the free amine gave values of 568 cm^{-1} and 177 cm^{-1} respectively and the values for the Zn, Cd and Hg compounds were in the ranges 634-623 cm^{-1} and 188-180 cm^{-1} respectively. This increased bond order of the Si-N bond was probably due to the combination of the empty d orbitals upon the silicon atoms

with the lone pair of electrons upon the nitrogen. This reduction of electron density on the nitrogen might then facilitate the reduction of electron density upon the cobalt atom.

The metal carbonyls and metal olefin complexes have increased stability by back donation of the metal d electrons to the antibonding π orbitals. This has the effect of increasing the metal carbon bond order but decreasing the carbon-oxygen or carbon-carbon bond order. This mechanism is not in operation in the bis-hexamethylsilylamino cobalt (II) because as shown the bond order of the nitrogen-silicon increases not decreases.

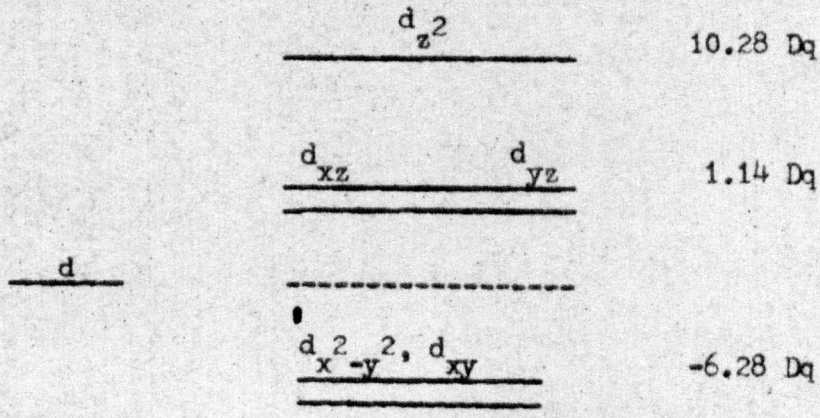
The strength of a cobalt nitrogen bond might be thought to be intermediate between a cobalt-oxygen bond and a cobalt-carbon bond. One very similar cobalt oxygen system which had been examined was the siloxy compound. $Co\left[OSi(CH_3)_3\right]_2$ which was thermally stable up to at least 180°C under vacuum[80]. The two alkoxides prepared in this thesis also appeared to be as thermally stable as the above compound.

Cobalt alkyls are unknown. Stable cobalt-carbon bonds are formed when there is a reduction of the electron density upon the metal atom. Stable alkyl (e.g. methyl) cobalt compounds are formed in the presence of ligands such as the porphins[81] and dimethylglyoxime[82].

Bis-hexamethyldisilylamino cobalt (II) was thermally stable being easily distilled in contrast to all other dialkylamides prepared which were unstable thermally. Whereas silicon has unfilled d orbitals to reduce the electron density upon the nitrogen, carbon does not have any available d orbitals and the inductive effect of the alkyl groups actually increases the electron density upon the nitrogen.

A full X-ray structural determination maybe required before definite conclusions maybe drawn as to the cobalt-nitrogen bond order. The compound is crystalline but because of the oxygen sensitivity a single crystal determination will be difficult. Also the stereochemistry in the solid may be different to that in solution (discussed in the next section).

The magnetic moment and visible spectra were not easy to explain. The energy level scheme for the d orbitals in a linear field is shown below. The Dq values assigned to each energy level are only correct for a system having a single d electron.



The bonds of M-X are assumed to lie along the z axis and so the d_{z^2} orbital is of highest energy. (Diagram above not to scale).

The value of the magnetic moment for the hexamethyldisilylamino cobalt (II) was found to be 4.84 B.M. at room temperature which indicated three unpaired electrons. Thus the d_{xz}, d_{yz} and d_{z^2} were assumed to each contain one electron. The spin-only value of the magnetic moment for three unpaired electrons being 3.88 B.M. suggested that the high value was caused by orbital contribution. Of course the energy level system shown above for the d^1 system need not hold for a d^7

system. Assuming that the arrangement of the energy levels was correct and that Dq was very small, then there was possibility of a large amount of spin-orbit coupling caused by mixing of the levels. This would increase the magnetic moment markedly from the spin-only value.

The magnetic moment in solution at room temperature was higher than that of the solid at room temperature. This high value was possibly due to three factors.

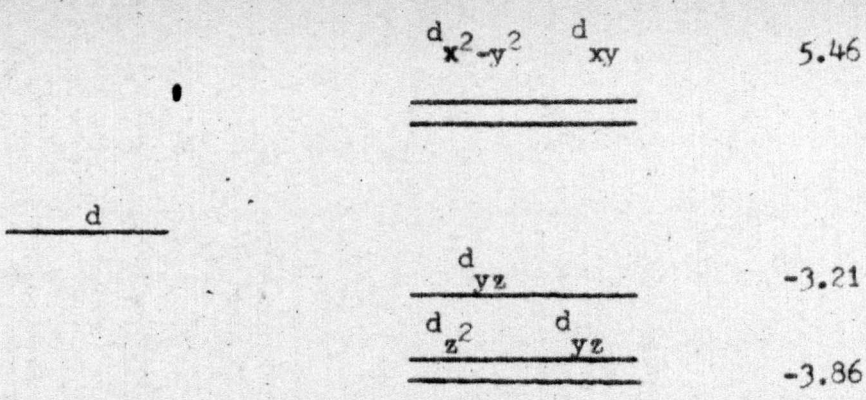
(a) Magnetic dilution in solution.

(b) A different coordination number in the solid from that in solution.

(c) Some oxidation to a spin-free cobalt (III) d^6 compound.

(a) If in the solid state there were magnetic interaction between cobalt atoms this would give a lower magnetic moment in the solid than in solution. The apparent temperature independence of the magnetic moment tended to rule out this possibility.

(b) The molecular weight in dilute solution, the volatility and I.R. spectrum in solution indicated a two coordinate cobalt system in solution and in the vapour phase but this did not rule out association in the solid phase. Although the hexamethyldisilylamide was a large bulky ligand, the possibility of higher coordination in the solid phase could not be ignored. Coordination with one further nitrogen and distortion of the linear N-Co-N system could have given a trigonal planar system. The energy levels of the d orbitals in a trigonal field for a d^1 electron system is shown on next page.

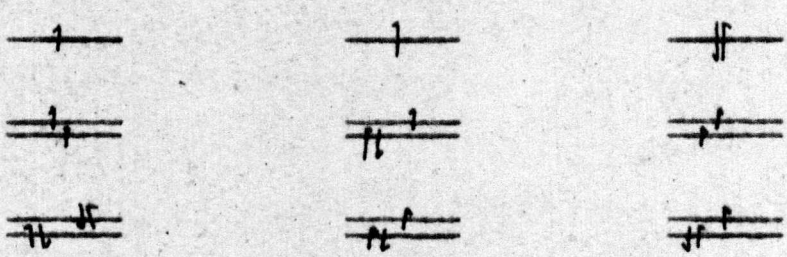


The trigonal field was assumed to be in the xy plane. Similar arguments used for a linear field may be used for a trigonal field in that a low value for Dq will cause large spin-orbit coupling and that the energy levels given for the d^1 system would not correspond rigidly with that expected for a d^7 system. A distorted tetrahedral structure (two long and two short bonds) may be possible but would probably be ruled out by steric hindrance.

(c) Although rigorous care was taken to exclude oxygen from the system and a strong solution (~15% w/w)was used, nevertheless oxidation could be a contributary factor. The bis-hexamethyldisilylamino cobalt (II) was shown to be very susceptible to oxygen being oxidized to a black cobalt (III) compound. If Dq were small then it would be possible to obtain a spin-free d^6 ion with four unpaired electrons. The increase in magnetic moment was possibly due to this effect although the solution was quite green and on exposure to oxygen turned black immediately. This route to a higher magnetic moment in solution was the least likely and may really be neglected.

A solution to the problem of whether the same coordination existed in the solid phase as did in solution may not be solved without a single crystal X-ray structural determination.

The U.V. and visible spectra were taken in solutions of pentane ($\sim 1.0 \times 10^{-3}$M) and because of the dilution of the solutions the quoted extinction coefficients were relative but absolute values were of limited value. The free ion terms for a d^7 ion are known but the terms that arise in a linear field were not known and so no real assignments can be made to transitions in the visible spectra. If we consider a strong field situation and a similar order of d orbital energies for the d^1 system then there are possibly two transitions.



Ground term First excited state Second excited state

Simply considering the ratios for the Dq values given for a d^1 system then the ratio of the energies of these transitions should be 7.42:16.56, i.e. 1:2:23. The ratio of energies of the two lowest energy bands observed was 10,650:17,100, i.e. 1:1.60. The agreement was probably of the right order but much more theoretical work must be done upon linear system before any real conclusions may be drawn from the electronic spectra and magnetic moment.

Because the other dialkylamides prepared were not easily purified and very oxygen sensitive, it was decided to prepare a derivative from the bis-hexamethyldisilylamino cobalt (II) and compare this with the derivatives obtained from the other dialkylamides. Generally metal

dialkylamides had been shown to react with alcohols to give alkoxides. The only known alkoxide of cobalt (II) which has been studied in detail was the methoxide[83]. This was shown to be octahedral with cobalt surrounded by six oxygens. It was decided to prepare alkoxides with larger steric hindrance in the hope of giving compounds with lower coordination. Tertiary butanol and triethylcarbinol reacted with bis-hexamethyldisilylamide and the 2,6-dimethylpiperidide to give similar alkoxides.

The alkoxides prepared gave visible spectra, as Nujol mulls, similar to cobaltous ions in aqueous solution $\left[Co(H_2O)_6\right]^{2+}$. Thus $\left[Co(H_2O)_6\right]^{2+}$ gave weak absorptions at 8,000 cm^{-1}, 19,600 cm^{-1} and 21,600 cm^{-1}, all these bands had molar extinction coefficients <5. "Dreiding stereomodels" of cobalt (II) tertiary butoxide showed that an octahedral cobalt (II) alkoxide cannot be formed with such large alkyl groups as $(CH_3)_3C-$ and $(C_2H_5)_2C-$. Winter[84] has recently shown that substitution of a methoxide group by a halogen in cobalt (II) dimethoxide caused interesting stereochemical changes. Thus the chloro-derivative $Co(OCH_3)Cl$ was found to be octahedral similar to the dimethoxide. The bromo derivative $Co(OCH_3)Br$ was shown to be tetrahedral but able to solvate with methanol to give an octahedral species. Solvation only occured with methanol and not with higher alcohols, showing that the tetrahedral species was preferred and only small ligands enabled the octahedral species to be formed. The iodo-derivative $Co(OCH_3)I$ was shown to be tetrahedral and did not solvate with methanol.

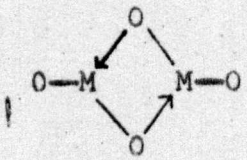
A solution of the triethylcarbinolate in tetrahydrofuran gave

a similar visible and near I.R. spectrum to the spectrum obtained in Nujol mull. The extinction coefficients were not measured but the weakest band at 8,300 cm^{-1} was shown to have an extinction coefficient greater than 50. This indicated that the stereochemistry was similar in tetrahydrofuran solution to that in the solid phase. There was a possibility that a change of stereochemistry did occur from the solid to the solution and the spectra were fortuitously similar. Much further work would be needed to prove this, e.g. magnetic moment of the solid.

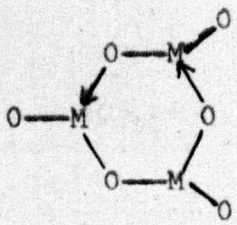
It will be initially assumed that there was no change of stereochemistry.

The magnetic moment of cobalt (II) triethylcarbinolate at room temperature was shown to be 5.04 B.M. This value indicated three unpaired electrons with a very high orbital contribution. It also indicated that the compound in solution was not tetrahedral. $Co(OCH_3)Br$ and $Co(OCH_3)I$ which were shown to be tetrahedral gave magnetic moments at room temperature of 4.69 B.M. and 4.83 B.M. respectively. The methoxy- group was shown to have a higher ligand field strength than a chloride group and so a triethylcarboxy- group should have a similar ligand field strength to a chloride group. The cobalt (II) triethylcarbinolate would probably have a magnetic moment of less than 4.69 B.M. if the stereochemistry of the cobalt were tetrahedral. Higher coordination than four may be discounted because of steric hindrance and the only possible stereochemistries are either square planar or trigonal planar. There have been no reported spin-free square planar complexes of cobalt (II). The

ligand field arising from triethylcarboxy- groups was not expected to be large enough to give a spin-free complex. A trigonal planar alkoxide of a bivalent metal may lead to two distinct stereochemistries as shown by Bradley[85]. These stereochemistries are dependent upon the oxygen-metal-oxygen angles. A bridging oxygen-metal-oxygen angle of 90° leads to polymers with a minimum degree of polymerization of two, shown below.



A bridging oxygen-metal-oxygen angle of 120° leads to polymers with a minimum degree of polymerization of three, shown below.



These alkoxides were insoluble in nonpolar organic solvents and soluble in tetrahydrofuran and the parent alcohols. Their low volatility and the similarity of the ditertiary-butoxide I.R. spectrum to that of zinc ditertiary-butoxide[86] indicated their polymeric nature. The exact degree of polymerization was not found, although if these compounds were similar to cobalt (II) bis-trimethylsiloxide (which sublimed at 180°C at 0.1 mm.Hg) then they would not have a very large degree of polymerization. A comparison with ferric triethylcarbonilate which was found to be monomeric, with a boiling point of 132°C at 0.1 mm.Hg,

indicated that it was possible to arrange three triethylcarboxy- groups around a cobalt atom (atomic radii Fe, 1.17 Å; Co,1.16 Å).

A much more detailed study of the chemical and physical properties of these compounds is needed before a stereochemistry may be assigned to the cobalt atom. The compounds may initiate the investigation of much more interesting chemistry of cobalt leading to further knowledge of how steric hindrance influences low coordination numbers.

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